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VOLUME 7, 1935

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ANALYTICAL EDITION

Industrial AND ENGINEERING Chemistry

VOLUME 7 NUMBER 1

JANUARY 15, 1935

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY

HARRISON E. HOWE, EDITOR

Statement of Policy and Note to Authors

THE ANALYTICAL EDITION has now completed six years of service, and those responsible for it have been pleased with its reception and with the realization that it has afforded encouragement to those working in this special field, at the same time placing a unique tool in their hands. With the record as a guide, we have formulated plans for further improving the edition. To that end a special Board of Associate Editors has been approved by the Directors of the SOCIETY, and six men have accepted service. The initial terms will be those indicated, at the expiration of which associate editors will be appointed for three-year periods. The following have been appointed:

B. L. Clarke, Bell Telephone Laboratories, 1 year
T. R. Cunningham, Union Carbide and Carbon Research Laboratories, 1 year
N. H. Furman, Princeton University, 2 years
I. M. Kolthoff, University of Minnesota, 2 years
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H. H. Willard, University of Michigan, 3 years

The board will assist in the formulation of policies, in the general improvement and usefulness of the publication, and will serve frequently as final referees in the critical examination of submitted manuscripts.

POLICY

The ANALYTICAL EDITION is primarily a journal for chemists specializing in analysis. In it will appear articles dealing with applications of methods of chemical analysis to problems primarily in industrial and engineering chemistry, though worthy papers in other fields may be accepted. Such articles will properly include apparatus and physical tests that are employed by the analytical chemist—for example, x-ray, colorimetry, chemical spectroscopy, calorimetry, and the like. Articles dealing more with the fundamental or theoretical considerations of no immediate application to chemical analysis belong more properly in the *Journal of the American Chemical Society*.

NOTE TO AUTHORS

In the preparation of manuscripts authors should address themselves to specialists in their particular fields, rather than to the general reader. If the article describes a new method, the author should endeavor to tell the complete story, so that the reader will not have to wait for succeeding contributions or duplicate the unpublished tests in order to find out whether he can apply the method in his own work.

The following is suggested as a general outline to be followed in preparing analytical methods for this edition:

1. Preliminary statement or introduction, in which the need for the method should be stated, brief reference to other methods or literature given, etc.
2. Experimental
   - Outline of proposed method
   - Description of apparatus and reagents
   - Procedure
   - Data
     - Interfering substances or conditions
     - Concentration range through which the method is applicable
     - Accuracy of the method
     - Precision of the method
3. Discussion and summary

The author should state at the outset why he thinks the paper is worth publishing. If it deals with a method of analysis, he should give some comparison with established methods in point of speed, applicability, accuracy, and cost. Extensive reviews of the literature should not be given and such references as are cited should be carefully checked. Incorrect references are inexcusable and cast doubts on the author's reliability. The theoretical considerations on which the method is based should be clearly set forth.

In the experimental part, previously published or well-known procedures which have been followed should only be designated or references given to them. If, however, the method is new, the data upon which it is based should be presented but in no greater de-

295055

tail than is necessary to prove its soundness. New procedures should be clearly described, that readers can easily duplicate the work. Loose directions should be avoided, unless the author knows that no possible harm can result from the most liberal interpretation that can be made of such expressions as "to the faintly acid solution," "wash the precipitate," "ignite," etc. If new or uncommon reagents are needed, the author should state their probable cost, where they can be purchased if rare, or how they can be prepared, if not on the market.

The author should distinguish carefully between precision and accuracy. Briefly but somewhat roughly stated, accuracy is a measure of degree of correctness; precision is a measure of reproducibility. The precision of a result does not necessarily have anything to do with its accuracy; it serves merely as a measure of the duplicability of the procedure in the hands of a given operator. No claim for accuracy should be made unless the author believes that he has satisfactorily established the correct result.

The author should be frank and define the limitations of the method. Tests dealing with the effects of foreign compounds should be made on mixtures in which the ratios of the compounds sought to the foreign compounds are varied and simulate conditions that are likely to be encountered in practice. If the author has made no such tests, he should state that he has no knowledge of the effects of foreign substances. It is desirable that possible applications of methods should be stated.

A summary or prefatory abstract should acquaint the reader with the main points of the article. This should give concisely where possible the substances determined, nature of material to which determination is applicable, interfering substances, range of concentration to which method is applicable, whether or not a sensible constant error is involved—that is, the accuracy of the method—and its precision. Either the summary or the prefatory abstract is so often used by abstractors that the author may well spend considerable time in their preparation, in order to be certain that proper emphasis is given to the main features of the contribution.

Our "Suggestions to Authors" is available to those unfamiliar with the form of manuscript and illustrations preferred by INDUSTRIAL AND ENGINEERING CHEMISTRY.

Microdetermination of Lead

Electrolytic-Colorimetric Method

MERLE RANDALL AND MARIAN N. SARQUIS, Chemical Laboratory, University of California, Berkeley, Calif.

IN A study of the solubility of lead sulfate in aqueous solutions of acetic acid it was necessary to determine accurately small amounts, 2 to 15 mg., of lead. From 95 to 99 per cent of the lead in solution was precipitated electrolytically as lead peroxide and the remainder was determined colorimetrically in the form of lead sulfide.

The solution to be analyzed was measured into an electrolytic beaker (9 cm. high, 3.8 cm. diameter) and 4 ml. of nitric acid (sp. gr. 1.42), 8 drops of 3 *M* sulfuric acid, and enough water to make the volume 35 ml. were added.

The anode was a small cylinder (4.5 cm. high, 1 cm. diameter) of fine platinum gauze, 40 mesh per inch (16 mesh per cm.) with a piece of platinum wire attached, and the cathode a spiral of platinum wire wound on a thin glass rod. The anode was secured by means of a gold-plated clamp, instead of the usual holder in which the end of a screw engages the electrode used for the cathode. It was found that the action of the screw against the electrodes caused a loss in weight of as much as 0.05 mg.

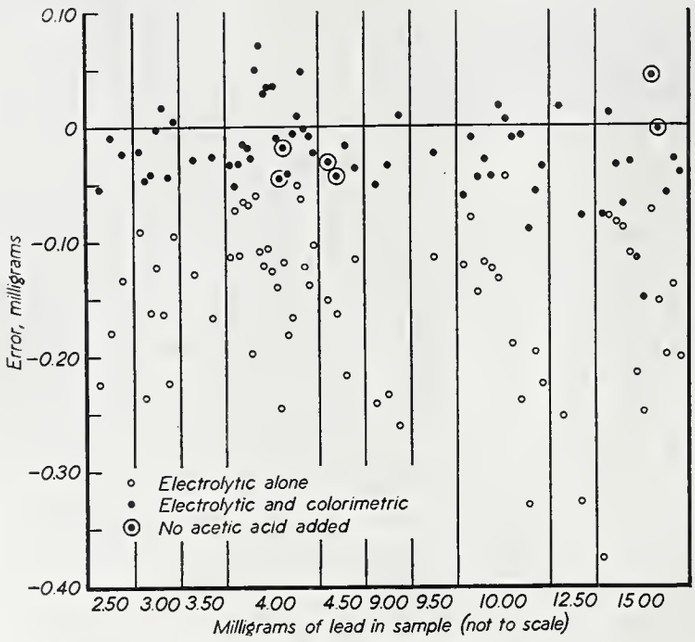


FIGURE 1. ERROR IN MICRODETERMINATION OF LEAD

The solution was electrolyzed for 12 to 18 hours at approximately 10 volts with a current of 0.05 ampere. Enough water was added so that, without breaking the circuit, the cathode could be lifted from the center of the anode and placed to one side of it. The current was short-circuited through the cathode and simultaneously the anode was taken out of the solution and rinsed well, first with distilled water, and second with absolute alcohol. The rinse liquids were collected in a casserole placed below the anode. The anode with its deposit of lead peroxide was then placed for 2 hours in an oven maintained at 180° C., after which it was allowed to come to equilibrium with respect to the temperature and moisture content of the balance case, and carefully weighed on a microchemical balance with a sensitivity of 0.005 mg. Tares were used, so that the rider alone was sufficient to weigh the deposit. The theoretical factor was used to calculate the amount of lead precipitated.

The procedure followed for the colorimetric determination was a combination of the methods employed by Francis, Harvey, and Buchan (*2*)

and Allport and Skrimshire (*1*). The reagents and materials were tested to prove the absence of lead and sulfide. The sodium sulfide solution was made as suggested by Francis, Harvey, and Buchan (*2*).

The solution remaining in the electrolytic beaker was poured into the casserole containing the liquids used in washing the anode, and the beaker and cathode were well rinsed. The solution in the casserole was then evaporated to a volume of 10 ml. over a steam bath. Any particles of lead peroxide which might have been present dissolved during the process. In the meanwhile, 2 ml. of 10 per cent potassium cyanide solution, 5 ml. of 6 *N* ammonium hydroxide, and 2 grams of ammonium acetate were placed in each of two exactly similar tall 50-ml. Nessler cylinders. The solution in the casserole was neutralized with 6 *N* ammonium hydroxide and transferred to one of the cylinders. Water to the 50-ml. graduation and 3 drops of sodium sulfide solution were added. Finally, the cylinder was shaken repeatedly until the ammonium acetate was dissolved and the solution was uniform. The other cylinder was treated similarly, except that a known amount of a lead nitrate solution, containing 0.01 mg. of lead per ml., was added instead of the solution from the casserole. After a little practice, it was easy to determine within 0.05 mg. the number of milligrams of lead present in the unknown solution by noticing the color intensity, and this quantity of lead was added to the standard cylinder for best comparison. The solutions were compared in a Leitz colorimeter.

The colorimetric value of the lead left in solution after electrolysis was in error from 5 to 20 per cent, but since this value was a small addition to the value determined electrolytically, the result was a considerable lowering of the total percentage error, which without the colorimetric correction was from 2 to 10 per cent.

The method was tested by analyzing measured volumes of a solution of lead nitrate containing 0.5 mg. of lead per ml., prepared by dissolving a weighed amount of pure test lead in nitric acid and diluting with water to the proper volume.

Since the method was developed for determining the lead content of solutions containing a small amount of acetic acid (left after several hours' boiling) a drop of glacial acetic acid was added to the known test solutions. A few of the solutions did not contain acetic acid (indicated in Figure 1) and it is readily seen that the presence of acetic acid in such small quantities did not affect the electrolytic precipitation of lead peroxide. With samples containing from 2.5 to 15 mg. of lead the deposit of lead peroxide adhered strongly to the anode and did not drop off even under vigorous shaking. The results of the various test analyses are summarized in Table I, and in Figure 1 the absolute error in milligrams of the individual analyses is indicated. The vertical sections of the chart show the total amount of lead in the various test solutions. The accuracy in the most unfavorable cases was about 1.5 per cent, and in the majority of cases it lay well below 1 per cent.

Table I. Microdetermination of Lead by an Electrolytic-Colorimetric Method

Lead Taken	No. of Experiments	Average Lead Found: Electrolytically	Average Lead Found: Colorimetrically	Error: Maximum	Error: Minimum	Error: Average
Mg.		*Mg.*	*Mg.*	*Mg.*	*Mg.*	%
15.00	12	14.836	0.13	0.149	0.003	0.29
12.50	2	12.210	0.26	0.078	0.017	0.37
10.00	12	9.821	0.13	0.090	0.006	0.34
9.00	4	8.753	0.24	0.034	0.021	0.24
5.00	1	4.884	0.08	0.036	...	0.70
4.50	3	4.324	0.15	0.043	0.017	0.68
4.00	21	3.882	0.12	0.071	0.002	0.72
3.50	2	3.353	0.12	0.028	0.026	0.77
3.00	7	2.844	0.14	0.043	0.002	0.83
2.50	3	2.321	0.15	0.054	0.009	1.2

Literature Cited

(1) Allport and Skrimshire, *Analyst*, 57, 440 (1932).
(2) Francis, Harvey, and Buchan, *Ibid.*, 54, 725 (1929).

Received November 8, 1934.

Determination of Selenium

Quantitative Determination on Animal Matter and Clinical Test in Urine

H. C. Dudley and H. G. Byers, Bureau of Chemistry and Soils, Washington, D. C.

Robinson, Dudley, Williams, and Byers (*1*) report procedures for the determination of selenium and arsenic in a variety of materials. These methods were developed in response to the necessities of an investigation of the selenium content of minerals, shales, soils, vegetation, and animal tissues and products.

Selenium has been found in the tissues and in the blood, feces, and urine of all animals which have ingested seleniferous food, and also in the milk of selenized cows, whether the cows have been fed seleniferous vegetation or have been given inorganic compounds of selenium. Selenium has also been demonstrated in eggs from selenized hens. The development of an accurate method of determination of selenium in these materials is essential for satisfactory work and a clinical test as an aid to diagnosis of selenium poisoning is urgently required. The procedures detailed in this paper are believed to be an advance upon those previously reported.

Quantitative Determination in Animal Tissues and Products

1. For blood, eggs, flesh, hair, bones, or hoofs, the quantity of material required is from 50 to 100 grams.

The material in a suitable state of subdivision is placed in a beaker (400 to 600 cc. capacity), covered with 150 to 200 cc. of concentrated nitric acid (sp. gr. 1.42), and allowed to stand at room temperature for from 2 to 3 hours, during which period it is stirred vigorously at intervals. Fifty cubic centimeters of hydrogen peroxide (30 per cent by weight) are added and the mixture is allowed to stand overnight. If frothing occurs on addition of the hydrogen peroxide, foaming over is prevented by vigorous stirring of the foam. The foaming is particularly intense with blood, liver, and spleen. After standing overnight, the mixture is warmed slowly on the steam bath until frothing ceases, after which 50 cc. more of hydrogen peroxide are added, together with 20 cc. of concentrated sulfuric acid. The mixture is then taken to essentially complete dryness on the steam bath or hot plate. The cooled black paste is treated with 100 cc. of hydrobromic acid (45 per cent HBr) to which has been added sufficient bromine to make it deep yellow in color. The material is then transferred to a distilling flask and 50 to 75 cc. of distillate are collected. Further procedure is as directed by Robinson et al.

2. For milk, the procedure is essentially as for other animal material, except that a quantity of from 500 to 1000 cc. is advised. The final evaporation should be carried out on a hot plate as soon as the fatty material has separated out as a clear yellow layer on the surface of the mixture. This fatty layer, which also appears with egg yolk and other fatty tissues, makes necessary the use of a hot plate for the complete evaporation.

3. The procedure for urine is similar to that for milk, ex-

cept that the sample may be as large as desired. The residual pasty material, if highly colored, may be decolorized by a third treatment with hydrogen peroxide.

An example of the application of these procedures is given in Table I, which illustrates the range of values obtained.

Table I. Selenium Content of Various Materials of Animal Origin

Lab. No.	Material	Selenium Content
		P. p. m.
B13724	Milk	0.02
13767	Milk	3.0
11814	Milk	0.5
13766	Milk	2.0
4327	Normal blood of pig	0.0
4328	Blood of pig	0.5
4328	Hoof of pig	2.0
7710	Liver of rat	4.7
7710	Kidney of rat	1.2
12347	Normal liver	0.0
13727	Heart of calf	16.0
13727	Blood of calf	27.0
13727	Liver of calf	25.0
13727	Lungs of calf	8.0
13726	Urine of cow	5.0
5796	Urine of pig	0.1
11813	Egg white	6.0
11813	Egg yolk	1.0
11813	Egg shell	3.0

Clinical Test for Selenium in Urine

Since selenium always appears in the urine of animals fed with seleniferous vegetation, a clinical test sufficiently accurate for detection of minute quantities and sufficiently simple to be used in a doctor's office or in a drugstore would be of great benefit as an aid to diagnosis in areas known to be affected by a selenium soil. The procedure outlined is relatively simple and is the best the authors have as yet been able to devise.

A quantity of urine ranging between 100 and 500 cc. is placed in a large beaker and treated with 25 cc. of concentrated nitric acid and 30 cc. of hydrogen peroxide (30 per cent by weight). If seleniferous vegetation has been consumed, normally 100 cc. is a sufficiently large sample. The mixture is slowly warmed, and if rapid evolution of gases threatens loss, the bubbles are broken by vigorous stirring of the foam. After foaming ceases, the mixture is evaporated to dryness on the steam bath or hot plate. If the residue is darker than a very light yellow, it is treated with 10 cc. of hydrogen peroxide and again evaporated to dryness. The dry residue is treated with 10 cc. of hydrobromic acid (20 to 25 per cent HBr) which is colored yellow with half a drop of bromine. Without warming, the solution is filtered through an asbestos felt filter into a test tube of colorless glass. To the filtrate is added 0.25 to 0.5 gram of sodium bisulfite ($NaHSO_3$) and it is then gently warmed for 15 minutes, and allowed to stand for from 1 to 3 days. A pink precipitate indicates the presence of selenium. If the coloration is but slight, it may be brought into sharper relief by examination in the sunlight by looking vertically into the tube. The time required for the formation of the precipitate is much less if hydroxylamine hydrochloride or hydrazine sulfate is available for reducing the selenium.

If any doubt exists as to the source of any color observed, it may be resolved by filtering the material through a fine asbestos filter, washing with water, and redissolving the pink coloration on the filter in from 3 to 5 cc. of hydrobromic acid which is rendered yellow by addition of bromine. The filtrate is reprecipitated with from 0.1 to 0.2 gram of sodium bisulfite (or with hydroxylamine hydrochloride). No pink color will be observed in the absence of selenium.

To test the validity of the method as outlined, 50 cc. of urine from a normal horse, which gave no test for selenium, were treated with 0.05 mg. of selenium as sodium selenate. No visible test was obtained on the first precipitation with sodium sulfite, but on addition of hydroxylamine hydrochloride a faint coloration appeared after standing 24 hours. Using 0.1 mg., however, the test was very pronounced, and reprecipitation as described recovered 0.08 mg. Horse urine is very highly colored and probably offers the maximum degree of difficulty in the application of the method.

No sample of seleniferous human urine was available, but a normal sample to which was added 0.05 mg. of selenium in 100 cc., as sodium selenite, gave a somewhat doubtful test in 24 hours. A very satisfactory test resulted when 0.1 mg. of selenium was used with 100 cc. of urine, and became clearly defined in 12 hours.

A cow which had been selenized furnished urine for the following tests: Ten cubic centimeters of urine containing 0.04 mg. of selenium gave a positive test after standing 12 hours. A 100-cc. sample, containing 0.40 mg., gave a clearly defined positive test in 1 hour.

It is unfortunate that no test directly applicable to untreated urine is available. When the attempt is made to apply the foregoing test without treatment with nitric acid and hydrogen peroxide, no satisfactory results were obtained, even by filtering and reprecipitation.

Literature Cited

(1) Robinson, W. O., Dudley, H. C., Williams, K. T., and Byers, H. G., Ind. Eng. Chem., Anal. Ed., 6, 274 (1934).

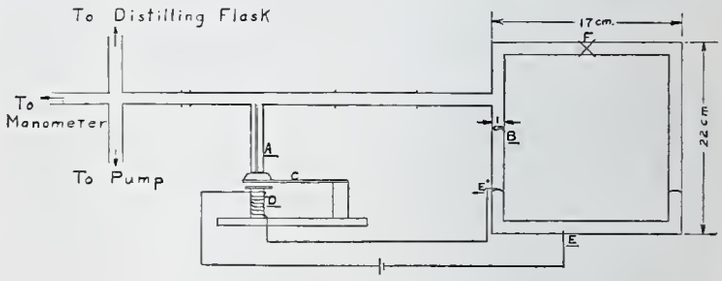
Received December 4, 1934.

An Inexpensive Vacuum Regulator

C. W. McConnell, Hyvis Oils, Inc., Warren, Pa.

The author's method of setting up an apparatus for what might be called a 100-mm. Engler fractionation may be of interest to lubrication engineers.

In the line is a glass T, one arm of which, *A*, is a small capillary used as a leak. This T joins the rest of the apparatus to a mercury gage, *B*. The leak on the T is covered by a piece of rubber or other suitable material mounted on a flexible steel spring, *C*, which acts as the armature for the small doorbell magnet, *D*. The bell or switch for the magnet is the mercury gage which is



pierced by two platinum wires, *E*,*E'*. When the apparatus is exhausted to the desired vacuum, stopcock *F* on the mercury gage is closed, the mercury rises, touches contact *E'*, and closes the magnetic circuit. Armature *C* is pulled down and opens the capillary leak, and the pressure within the apparatus is kept constant to within at least the accuracy of a mercury manometer. Obviously, gage *B* is so adjusted that contact *E'* just fails to touch the mercury when stopcock *F* is open.

The apparatus is inexpensive—a couple of dry cells, the glass T, some wire, a doorbell, and an alarm clock spring are easily obtainable and leave the cost of the mercury gage the only expense.

The Petroleum Research Laboratory at the Pennsylvania State College is, so far as the author knows, the originator of the apparatus, but he believes that only his laboratory has fully utilized its really remarkable flexibility.

Received September 24, 1934

Accelerated Tests of Paint Finishes on Aluminum

Junius D. Edwards and Robert I. Wray, Aluminum Company of America, New Kensington, Pa.

An accelerated test of paint finishes on aluminum, which includes periodic immersion in salt water followed by atmospheric exposure in predetermined cycles, has been found useful in investigating painting practice on seaplanes. The apparatus consists of large wooden tanks which are automatically filled with salt water at definite intervals. Boxlike structures of the aluminum alloy 17S-T were used as test specimens, exposed in the tank in such a manner as to be completely wet, inside and outside, when the tanks were filled. The results secured closely parallel the types of failure experienced in service.

An investigation of various surface preparations showed the following order of excellence: anodic coatings, oxide coatings produced by means of chemical dips, treatment with phosphoric acid solutions, treatment with phosphate solutions, and cleaning with solvents.

Investigations of types of painting systems indicate that the best finishing system found to date involves the use of an anodic coating and a phenolic resin–base zinc chromate primer applied and dried before assembly, followed by aluminum paint made with the same type of vehicle.

The difficulties in the way of developing satisfactory accelerated tests for paint finishes are generally recognized. Nevertheless, the need is so urgent that their use is justified, providing the results bear some reasonable relation to service performance.

In the use of thin aluminum alloy sheet on seaplanes, particularly on pontoons, service conditions are met which may require paint protection. In and out of sea water, alternately wet and dried, paints on seaplanes are put to a searching trial. In examining paints for this service, a test has been developed which gives good results and has yielded valuable information. A description of this test, which has been in use since 1926, and some of the information gained from it are presented because it seems generally applicable to paints for metal which is subject to wetting and drying in service.

Description of Apparatus

The test consists of immersion in salt water for a set period, followed by exposure to the atmosphere and drying; the two conditions are repeated in cycles. The test apparatus, shown in Figure 1, is located on the roof of a factory building at Edgewater, N. J.

Three large open wooden tanks approximately 12 feet long, 4.5 feet wide, and 18 inches deep contain the test specimens. A large water-supply tank located at the side and above the first tank furnishes the water for filling the test tanks. Water from the Hudson River is pumped directly into the supply tank. A typical analysis of this water, made in August, 1932, was as follows:

	G./l.
Cl	10.4
SO_4	1.4
CO_3	0.065
pH	7.9

The water contains approximately 1.7 per cent of sodium chloride, about half the concentration found in sea water.

When the water reaches a predetermined level in the supply tank, a large float trips a valve, permitting the water to flow into the uppermost test tank and fill it to a level about 3 inches above the specimens. As the tank fills, a similar float rises until it trips a valve in this tank, the water flowing to the next tank and so on to the last tank, from which it is discharged into the river. It usually requires about 40 minutes to fill the supply tank and about 10 minutes to drain it. The specimens are thus immersed for about 10 minutes and are out of the water until substantially dry during each cycle. A new supply of water is used in each cycle, since the old water is returned to the river.

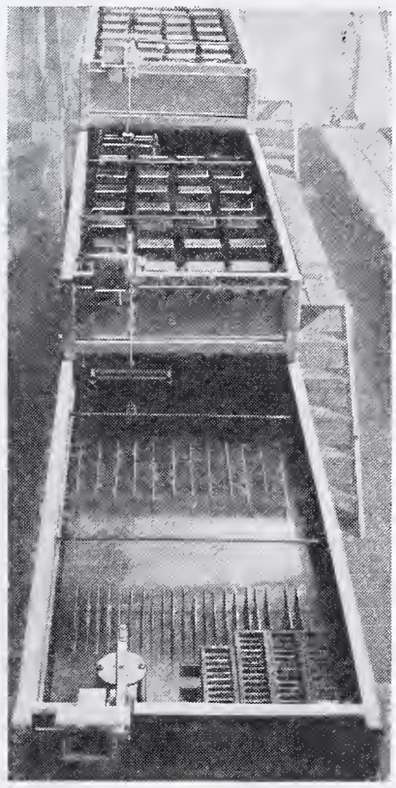


Figure 1. Test Apparatus

This apparatus can, of course, be operated only during the months when there is no danger of freezing, normally from about the middle of April until the last of November. For many coatings this period has been sufficient to produce substantial breakdown. Specimens which successfully withstand one season's exposure are returned to the tanks the following year and the test is repeated until failure occurs or the answer is obtained to the problem under investigation. The test specimens are generally stored indoors between exposure periods. In a few instances specimens have been continued in the test for 5 years.

Various types of specimens can be exposed in these tanks, but experience has shown that the most comprehensive information can be secured by the use of a fabricated specimen containing riveted or welded joints and parts never exposed to the sun, simulating conditions inside a pontoon. In the earlier tests a fairly complicated specimen was employed (Figure 2) which embodied joints of dissimilar metals, metal-to-wood, etc., such as might be used in aircraft construction. Although much valuable information was secured through its use, the number of tests which could be made at one time was limited because of its size and design. Consequently a much simpler specimen was adopted, consisting of a boxlike structure with riveted sides, open at the bottom and vented at the top. This box was 10 inches high, 10 inches long, and 7 inches wide, and was fabricated from Aluminum Company of America's alloy 17S-T sheet; this is a heat-treated alloy similar to duralumin in composition and proper-

ties, which is widely used in aircraft construction. About one hundred of these boxes can be exposed in the tanks during one season. By exposing them open end down, the inside fills with water as the tanks fill; the inside is thus always exposed to a very humid atmosphere and is never thoroughly dried, whereas the outside is alternately exposed to sunlight and salt-water immersion. The boxes are supported in the tank so that the lower 2 or 3 inches of specimen are continuously immersed in the water which does not drain from the tank. This permits a study of paint behavior at the water line, which is generally recognized to be a critical point. It has also often been found that the moisture conditions inside the box produce more rapid failure here than on the outside of the box.

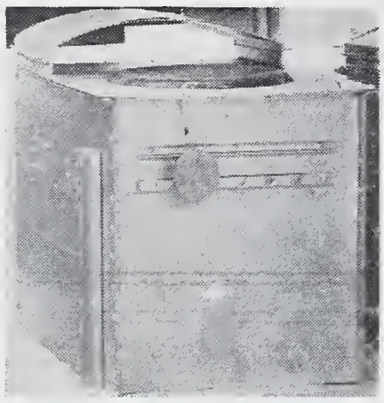


Figure 2. Early Type of Test Box

Where a large supply of sea water or brackish water is not available, as at New Kensington, another expedient is employed. The test pieces are carried on a frame which, by mechanical means, is alternately raised from the tank and lowered in predetermined cycles. For other purposes, such as the testing of paints to be used on boats in fresh water, fresh water could be used in the tanks.

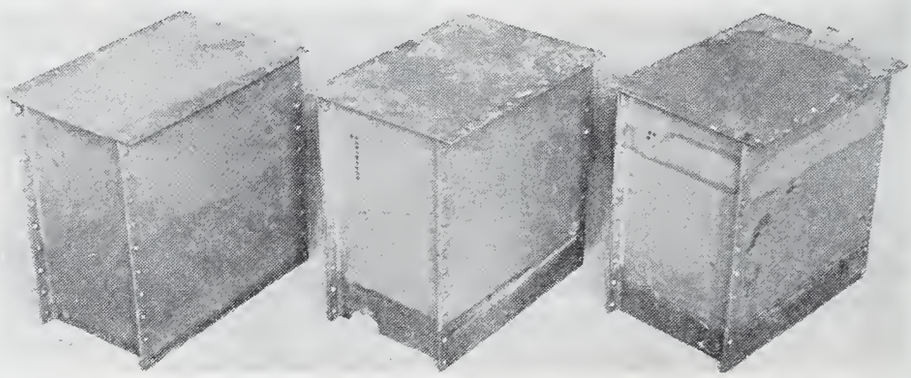


Figure 3. Effect of Surface Preparation

Test boxes of 17S-T alloy, coated with two coats of aluminum paint, after one season's exposure. Box on left treated with phosphoric acid, others with sodium phosphate-type cleaners before painting.

Investigation of Surface Preparation

As with other metals, the preparation of the surface of aluminum alloys is a very important step in securing satisfactory paint service (*1*), particularly under the severe conditions of exposure to which seaplanes are subjected.

The simplest type of surface preparation is that of solvent cleaning to remove oil and grease. Test and experience show that this treatment is quite insufficient for this type of service. Even with the most durable coatings, the paint blistered and peeled from the solvent-cleaned surface within one season's exposure in the alternate immersion test. Less durable coatings showed failure within a month or two.

Certain chemical treatments were found to give much better results than solvent cleaning. The most common materials used for this purpose contain either phosphates or phosphoric acid. The phosphate cleaners are normally used as aqueous solutions, while cleaners of the latter type usually contain a solvent such as alcohol to assist in the removal of grease. The phosphoric acid or phosphate apparently reacts with the aluminum surface, forming a very thin film of aluminum phosphate which renders the metal passive—less reactive to moisture. Of these two, the phosphoric acid type of cleaner has been proved to be the most effective. Although these materials are generally referred to as cleaners, their chemical action on the metal is at least as important as any effect they have in removing dirt and grease.

In one series of tests a number of boxes were cleaned with different chemical cleaners, thoroughly rinsed in running water, dried, and coated with two coats of aluminum paint. After one season's exposure, the paint on all boxes had shown definite signs of failure, but the boxes cleaned with phosphoric acid cleaners were in noticeably better condition than those cleaned with phosphate. Three of these boxes are shown in Figure 3. The box on the left was cleaned with a phosphoric acid cleaner containing alcohol; the top face showed some paint peeling but the paint on the sides was almost intact. The middle box, cleaned with a moderately alkaline sodium phosphate cleaner, showed bad paint blistering and peeling from the top with many large blisters and peeled areas on the sides. The box on the right was cleaned with a sodium phosphate cleaner of less alkaline characteristics, the paint showing similar failure to that of the middle box.

The best results in the way of surface preparation are secured by means of anodic oxidation. There are two methods in general use for applying such coatings: anodic coating in a chromic acid solution, and the Alumilite process of anodic coating in sulfuric acid solutions. Practically no difference has been found in the results secured with these two methods as surface preparation for painting. Both surfaces have proved to be excellent bases for paint for severe exposure conditions. The box in Figure 4 was anodically coated in a chromic acid solution and given two coats of aluminum paint. It was in excellent condition even after 2 seasons' exposure. A similar box anodically coated in sulfuric acid solution and painted in the same way was also in excellent condition after a like period. Another pair of boxes having the same treatment was in very good condition after 3 seasons' exposure. Paints over anodic coatings have lasted as long as 5 seasons in this test. The box shown in Figure 5 has been in the test for 5 seasons. It was anodically coated in chromic acid solution and painted with a linseed oil–base zinc chromate primer and one coat of aluminum paint.

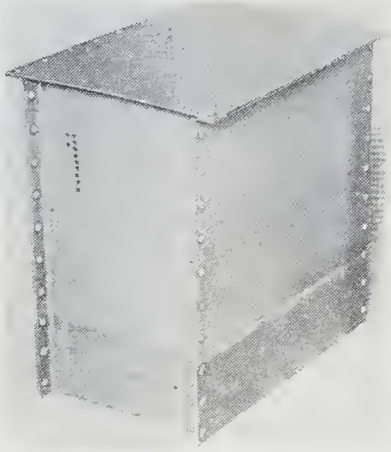


Figure 4. Anodically Coated 17S-T Alloy Test Box after 2 Seasons' Exposure

Two coats of aluminum paint.

Investigation of Paints on Aluminum

In selecting a satisfactory primer for aluminum seaplanes, both the pigment and the vehicle have been found to play an important part. Of the pigments tested as primers, iron oxide by itself proved rather ineffective, red lead was not found satisfactory under

the test conditions, while aluminum bronze powder proved fairly effective. The chromate pigments were definitely better than any of the other pigments tested. Of the chromate pigments, zinc chromate gave decidedly the best results, regardless of the type of vehicle employed. Zinc chromate shows decided inhibitive properties in priming coats on aluminum; this may be ascribed to its soluble dichromate content. Even small amounts of dissolved potassium dichromate in salt water have been found to stop corrosion on aluminum surfaces.

FIGURE 5. ANODICALLY COATED 17S-T ALLOY TEST BOX AFTER 5 SEASONS' EXPOSURE

Oil-base zinc chromate primer and one coat of aluminum paint.

Combinations of zinc chromate and red oxide of iron, such as that described in U. S. Navy Proposed Specification P23b, while not generally as good as zinc chromate alone, have given very good results, better than those obtained with basic lead chromate alone or in combination with other pigments. Zinc chromate in combination with other pigments has some advantages over zinc chromate alone, such as better hiding and lower cost, and under some conditions can be used to good advantage.

For water immersion, particularly salt-water immersion, the vehicle of the primer must possess a high degree of moisture-impermeability. Tests have shown that some of the synthetic resin varnishes, particularly some of those containing phenolic resin, possess very high impermeability to moisture (*3*). The vehicle must also show good adhesion to the surface. The best painting procedure is logically to put the metal surface in as nonreactive condition as possible and then apply a durable series of paint coatings of minimum permeability to moisture.

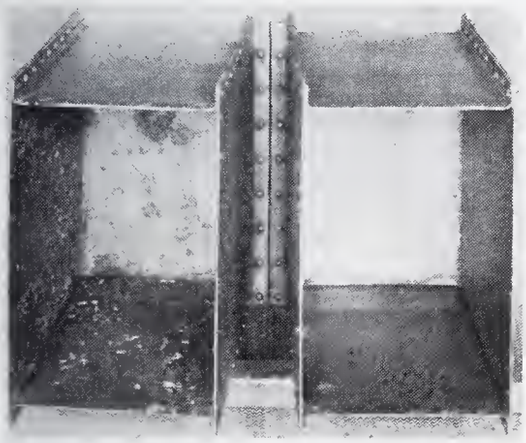


FIGURE 6. INTERIOR OF TWO ALUMINUM-PAINTED 17S-T ALLOY TEST BOXES AFTER ONE SEASON'S EXPOSURE

Spar varnish vehicle used on box on left and phenolic resin varnish on box on right.

In a series of tests conducted in 1932, aluminum paint primers made with several different types of varnish were compared. Paint made with an ordinary 80-gallon ester gum spar varnish showed rather bad failure in one season's exposure, whereas aluminum paint made with a phenolic resin varnish gave very good results, with the exception of some blistering near joints. The interior of these boxes is shown in Figure 6 and illustrates the type of failure observed.

These tests were partially repeated the following season, using primers made with zinc chromate. Although much less failure was observed in all cases, the phenolic resin–base primer again gave the best results, a glycerol phthalate–base zinc chromate primer being a close second. The former showed no failure after one season's immersion.

Tests made to determine the effect of applying the primer before and after assembly invariably showed that less failure occurred in joints which were protected by the priming coat applied and allowed to dry before assembly. Riveted joints cannot be made absolutely water-tight mechanically, and therefore should be protected with paint if possible.

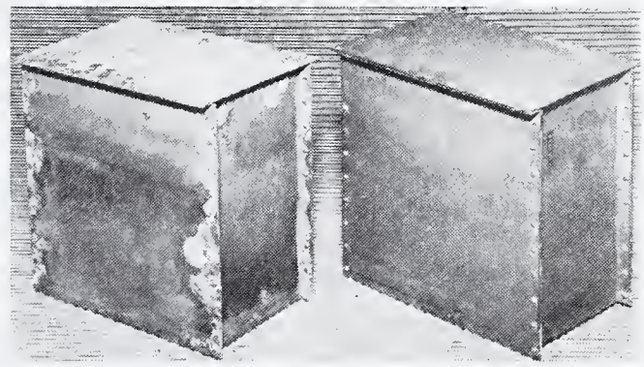


FIGURE 7. COMPARISON OF LACQUER AND SYNTHETIC RESIN–BASE ENAMEL

17S-T alloy test boxes treated with phosphoric acid-type cleaner, after 2 seasons' exposure.

The selection of finishing coats of paint for aircraft work is also governed by their moisture-impermeability and adherence and, in addition, their resistance to sunlight. Here again the proper selection of both pigment and vehicle is highly important. Of the various pigments tested, aluminum bronze powder has been found to give the most satisfactory results. This might be expected, since aluminum paint shows excellent moisture-impermeability and is but little affected by sunlight. Its adherence to the priming coat is generally very satisfactory. The vehicle used, however, is quite important. Synthetic resin–base varnishes gave the best results in aluminum paint when used as primers; this also applies to the finishing coats.

Some pyroxylin lacquers pigmented with aluminum bronze powder have also given very good results when applied over a suitable primer but pyroxylin lacquers as a group were found to be inferior to synthetic resin enamels. This was confirmed by Whitmore (*2*). In Figure 7 two boxes are shown, illustrating the greater durability of the synthetic resin enamel after 2 seasons' exposure. The box on the left was finished with a green pyroxylin enamel, one of the best tested, while the one on the right was finished with a green synthetic resin enamel employing the same type of pigment. Very little failure occurred on the box coated with synthetic resin enamel, whereas the lacquer-coated box failed rather badly at all joints and edges. The box shown in Figure 8, which was in practically perfect condition after 2 seasons' exposure, was finished with aluminum paint made with a synthetic resin varnish applied over a synthetic resin–base zinc chromate primer.

The effect of drying time between coats of paint or before immersion after applying the final coat is a very important consideration. This factor was not thoroughly investigated in these tests, as it was believed that allowing a sufficient drying period would eliminate the variable of drying time. It has been shown in other tests, however, that paint tends to become more impermeable as the film hardens. In many instances about one month may elapse after the finishing of

a plane before it is placed in actual service. An average of a month's drying time was also allowed after applying the final coat of paint to the test specimens before starting the test; from 1 to 2 weeks' drying time was allowed between coats. In tests of this kind it would be desirable to investigate varying drying periods, in order to establish the minimum drying time allowable.

It is difficult to state what one season in the accelerated test means in years of service, because service conditions vary so widely. However, comparative tests have been made with many of the coatings, both in air exposure and in the accelerated test described. For example, two coats of aluminum paint made with an 80-gallon ester gum spar varnish, which showed failure on 17S-T in one season (5 months) in the accelerated test, have shown only beginning failure after 3 years of normal atmospheric exposure on panels exposed at an angle of 45° facing south. In another case, an oil-base iron oxide primer followed by one coat of aluminum paint had begun to show failure in 2 seasons in the accelerated test, whereas a similar coating exposed to normal air conditions was still intact after 3 years' exposure. The green pyroxylin lacquer previously mentioned, which was still intact after 3 years' atmospheric exposure, had begun to show some peeling with corrosion of the metal after one season in the accelerated test; green synthetic resin enamel showed similar results. In a general way, it can be said that exposure for one season in the accelerated test is equivalent to 3 years or more of exposure under the atmospheric conditions prevailing at New Kensington. Coatings which last longer than one season in this test would be expected to possess very long life under land service conditions.

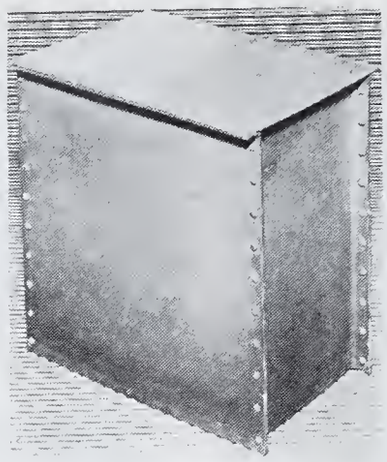


FIGURE 8. TEST BOX OF 17S-T ALLOY AFTER 2 SEASONS' EXPOSURE

Treated with phosphoric acid cleaner, followed by synthetic resin-base zinc chromate primer, followed by synthetic resin-base aluminum paint.

ACKNOWLEDGMENT

The original design and assembly of the test apparatus described in this paper were worked out in 1926 by members of the Technical Direction Bureau of Aluminum Company of America, especially E. Blough, C. F. Nagel, Jr., and F. V. Hartman, with the assistance of the engineering staff of the Glenn L. Martin Company.

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RECEIVED September 19, 1934. Presented before the Division of Paint and Varnish Chemistry at the 88th Meeting of the American Chemical Society, Cleveland, Ohio, September 10 to 14, 1934.

A Rapid Method for Dialyzing Large Quantities of Protein Solution

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DURING the course of preparing large quantities of pure proteins, it was found necessary to dialyze batches of 5 to 10 liters of the colloidal ampholytic solutions. The simple apparatus herein described was designed to carry out the dialyzing process efficiently.

Figure 1 shows a container of capacity sufficiently great to hold the protein solution. Pieces of 5-cm. (2-inch) tubular Cellophane, of about 25-cm. (10-inch) length, are folded at one end and clamped closed by means of screw clamps, fitted with two-hole rubber stoppers and bent glass tubes, and connected in series. They are placed in the protein solution in the crock, and cold tap water is run through them. The weight of the screw clamp is sufficient to keep the water-filled bags submerged in the solution. After most of the electrolytes have been removed from the protein solution, a slow stream of distilled water is run through the bags instead of the tap water.

The solution in the crock is kept in motion by means of a slow-moving stirrer, motor-operated, and fitted with a good-sized paddle. The solution may be preserved with toluene, chloroform, or thymol, the rapid evaporation of which is prevented by covering the crock with a large piece of cardboard perforated by the necessary holes.

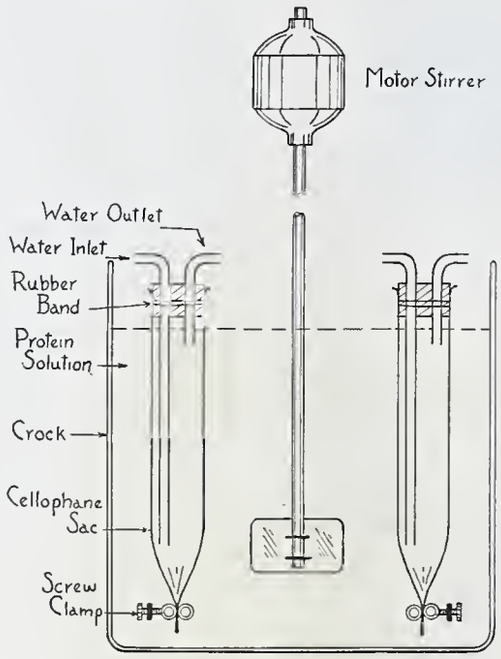

FIGURE 1

Because of the continual motion of the solution and the constant flow and removal of the dialysate, the process is rapid. Tubular Cellophane is easily obtained, and when wet is very strong. Breakage of the sacs, due to internal pressure such as may occur in the usual methods of dialysis where the medium to be dialyzed is placed within the sac, is eliminated, because in this case the water passes out of the bags into the solution.

It was found that 10 liters of a solution consisting of a protein dissolved in 10 per cent ammonium sulfate could be freed from the salt, as far as possible by ordinary dialysis, in the above apparatus in 24 hours—18 with tap water and 6 with distilled water.

The author is indebted to C. A. Marlies for helpful suggestions.

RECEIVED October 4, 1934.

Determination of Methane by Catalytic Oxidation

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THE danger of explosion constitutes a serious objection to the use of the slow-combustion method for the determination of methane when carried out by one who infrequently uses this procedure. Attempts have been made to increase the safety factor by modifying the pipet, but Steacie's method (*5*) is not suited to use in standard gas analysis, while Kobe's modification (*4*) lacks the necessary mechanical stability.

The Jager method (*3*), besides necessitating the use of a quartz combustion tube, requires such prolonged heating at high temperature that the process becomes too laborious. This method does not meet with the approval of some authorities (*2*).

The results of the recent work of Yant and Hawk (*6*) indicate that methane at comparatively low temperatures and space velocities can be completely oxidized in the presence of suitable catalysts. The possibility of adapting these reactions to analytical work offers a problem worthy of investigation. It is the purpose of this paper to show that catalytic oxidation of methane provides a safe and reliable method of analysis.

Apparatus

A Burrell Bureau of Mines gas-analysis apparatus (*1*) was used in this work. A pipet equipped with a three-way stopcock, mounted next to the slow-combustion chamber, made it easier to flush the system and provided an additional gas reservoir. The original furnace was replaced by one which could be maintained at a constant temperature through a range of 600° C.

A platinum–platinum-rhodium thermocouple incased in a Pyrex glass tube was mounted closely adjacent to the catalyst chamber with the junction at such a point that it accurately measured the temperature to which the catalyst was subjected. The construction of the furnace was such that the temperature was constant within ±5° C. over a range of 8 cm.

Two types of combustion tubes (simple and compound) were used. The compound tube was made by replacing one arm of an ordinary copper oxide tube with a catalyst chamber. One side then contained the copper oxide and the other the catalyst. The chamber finally adopted was 7.5 cm. in length and 3.5 cc. in volume.

The simple combustion tube consisted of merely the catalyst chamber, the copper oxide arm being replaced by capillary tubing.

Preparation of the Catalyst

Previous investigation (*6*) indicates that cobalt oxide under suitable conditions might serve as a catalyst for the oxidation of methane. Though cobalt oxide preparations gave high efficiencies, it was found that adsorption of carbon dioxide at 300° C. made them unsatisfactory for analytical purposes. This difficulty was overcome, however, by mounting a thin layer of the oxide on unglazed porcelain particles. As shown in Table I, the adsorption was in this manner rendered negligible.

The tests for adsorption were made by filling the combustion tube with carbon dioxide at 300° C. The tube at this temperature was carefully flushed out with nitrogen until it was apparently free of carbon dioxide. The temperature was then raised to 600° C., the tube was again flushed, and the carbon dioxide determined. Previous work had shown no adsorption at 600° C.

The catalyst finally adopted was made by the evaporation and subsequent thermal decomposition of a solution containing 1.2 grams of $Cu(NO_3)_2 \cdot 3H_2O$ and 14 grams of $Co(NO_3)_2 \cdot 6H_2O$ on 40 grams of 10-mesh unglazed porcelain particles. Attempts to coat this oxide on copper oxide wire resulted in an inferior catalyst.

Table I. Adsorption Tests

Sample	Amount of Catalyst	Total Cobalt Recovered at 600° C.
	Cc.	*Cc.*
1[a]	1.0	0.20
2	7.0	0.05
2	3.5	0.00

[a] The porcelain particles of sample 1 carried a much heavier coating of oxide.

Optimum Conditions of Catalysis

In order to determine the optimum conditions for the oxidation of methane, the effect of space velocity on catalytic efficiency was first studied. Results given in Table II are from runs made over 3.5 cc. of catalyst at 500° C., using a mixture of 15 per cent of methane and 85 per cent of oxygen. Since a rate of 20 to 25 cc. per minute is essential for rapid analysis, these results indicate that the use of a smaller volume of catalyst would not be advisable. In all subsequent tests 3.5 cc. of catalyst were employed.

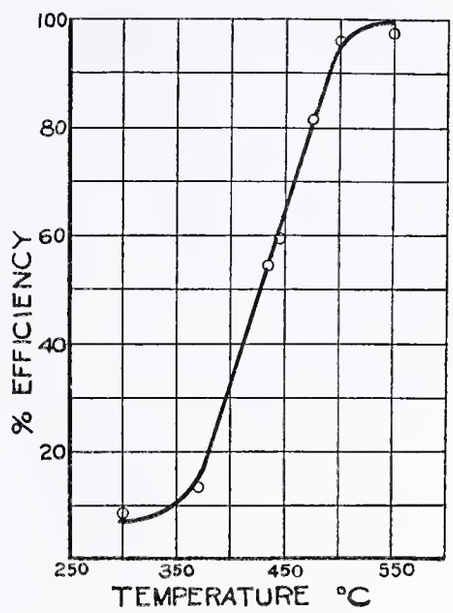

Figure 1. Influence of Temperature on Efficiency of Catalyst

As shown in Figure 1, temperature exhibits a very marked influence on efficiency below 500° C. These tests were made at 20 cc. per minute, using a mixture of 15 per cent of methane and 85 per cent of oxygen. The points given in the curve were taken from a single run in the order of descending temperatures. Points on the upper part of the curve were readily duplicated with different batches of catalyst. In the lower portions of the curve where conditions were obviously unfavorable, only qualitative agreement was obtained, but the curve represents the general trend of all such observations.

Table II. Efficiency of Catalyst

Rate	Space Velocity	Efficiency[a]
Cc./min.		%
10	168	98
30	500	97
40	666	94
60	1000	89
90	1500	84
120	2000	76
240	4000	63

[a] Efficiency means the percentage of methane oxidized in one passage over the catalyst.

To determine the effect of concentration, samples containing varying percentages of methane in methane-oxygen mixtures were passed over the catalyst at 20 cc. a minute and 500° C. Table III summarizes the results of this study, which indicate that up to concentrations approaching one part of methane to three of oxygen high efficiencies are maintained.

Table III. Effect of Concentration

Methane in Methane-Oxygen Mixture	Efficiency
%	%
4.4	98.0
7.4	98.7
14.1	98.5
22.1	96.8
23.4	97.1

Life tests made on the catalyst showed that after passage of 8 liters of a mixture of 15 per cent of methane and 85 per cent of oxygen (equivalent to eighty determinations in ordinary gas analysis) the efficiency had not changed. These results were duplicated using a 20 per cent methane mixture.

The data of Table III, which show a combustion of 97 per cent of the methane in the methane-oxygen mixture with only one passage over the catalyst, indicate that twice over the catalyst at suitable conditions, followed by flushing at 550° C., should insure complete oxidation.

Determination of Methane in Methane Residues

In standard gas analysis, methane is determined by the low combustion of an aliquot portion of the gaseous residue which remains after the other components (carbon dioxide, carbon monoxide, hydrogen, oxygen, and illuminants) have been removed. These residues are usually mixtures of nitrogen and hydrocarbons (methane). Since ordinary methane residues contain nitrogen, which is not considered in Table III, the effect of nitrogen as a diluent was studied. Preliminary work with methane-air mixtures had already shown under favorable conditions (low space velocities at 550° C.) a high degree of combustion. A summary of this work is given in Table IV. These results confirm the work of other investigators (*6*).

Table IV. Determination of Methane in Methane Residues

Sample	Methane in Methane-Air Mixture	Efficiency
	%	%
1	3.8	95
2	6.2	99
3	6.8	99
4	9.9	95

Since nitrogen even in high concentrations apparently has no effect on efficiency of combustion, catalytic oxidation suggests itself as another method for the determination of methane in methane residues.

Table V. Comparative Tests

Sample	Methane in Methane Residue	
	Slow combustion	Catalytic oxidation
	%	%
1	3.5	3.4
2	8.6	8.3
3	13.9	13.6
4	15.4	15.3
5	15.3	15.4
6	27.9	28.2
7	40.5	40.3
8	56.0	55.7
9	69.6	69.8
10	89.3	89.3

As a final substantiation ten methane residues (methane-nitrogen) containing from 3.5 to 89.3 per cent of methane were made up. Comparative tests with the slow-combustion method were made, employing 20-cc. samples, and using 60 to 80 cc. of oxygen for each combustion. Although in most cases this would be more oxygen than is necessary, it is well to provide sufficient gas for flushing. Results are tabulated in Table V and show complete agreement at all concentrations of methane ordinarily encountered in gas analysis.

Modifications of Procedure

To adapt this method to standard gas analysis apparatus two modifications present themselves:

1. One may employ two furnaces, one operating at 300° C. with a copper oxide tube for the determination of carbon monoxide and hydrogen, and the other operating at 550° C. with the simple catalyst tube for the determination of methane in the gas residue.
2. One may employ a single furnace capable of operating at variable temperatures, using only a compound combustion tube containing both the copper oxide and the catalyst. Since it previously had been found that methane did not reduce the catalyst at the temperature of use and that carbon dioxide was not adsorbed at 300° C., the use of one furnace involves only a slight modification in procedure. In this case after the oxidation of carbon monoxide and hydrogen, the combustion tube should be flushed and the carbon dioxide absorbed. Then the system should be cooled to room temperature and the hydrogen determined by contraction. (When the compound tube is used, it is necessary to reoxidize the copper oxide before proceeding with the analysis of the methane residues.)

To show that the compound combustion tube gave reliable results for the determination of carbon monoxide and hydrogen in the presence of methane, comparative tests were made with an ordinary copper oxide tube. These analyses (Table VI) were made on samples containing a mixture of carbon dioxide, carbon monoxide, methane, oxygen, hydrogen, and nitrogen.

Table VI. Comparative Tests

	Sample 1		Sample 2		Sample 3	
	CuO	CuO + catalyst	CuO	CuO + catalyst	CuO	CuO + catalyst
	%	%	%	%	%	%
Carbon dioxide	0.8	0.8	0.2	0.2	0.2	0.2
Oxygen	9.3	9.4	8.4	8.3	8.4	8.5
Hydrogen	19.1	19.2	21.8	21.9	22.1	22.3
Carbon monoxide	9.9	10.0	14.9	15.0	14.9	14.7
Methane residue	60.9	60.5	54.7	54.6	54.4	54.3

Comments

No difficulty was experienced in reproducing the catalyst. Three separate preparations were used throughout this work. Later experiments have shown that the amount of copper oxide (up to 50 per cent) incorporated in the catalyst had no effect on its activity.

Gaseous hydrocarbons such as Flamo (principally butane), a by-product of the Standard Oil Company of California, were completely oxidized under the conditions specified as suitable for methane. To insure no change in catalytic efficiency when oxidizing butane, lower space velocities should be used. It is evident that the presence of ethane and propane would have no effect on the catalysis.

Though the presence of moisture does not affect efficiencies, wetting the catalysts with other confining liquids renders them unfit for further use.

Traces of sulfur (1 part in 100,000) were found to poison the catalysis slowly. Since it is highly improbable that the gas after being subjected to the reagents used in standard gas analysis preliminary to the methane determination would contain the ordinary catalytic poisons, this phase of the subject has not been thoroughly investigated.

Summary

Catalytic oxidation offers a rapid, satisfactory, and safe method for the determination of methane in gas residues.

Methane in methane residues was quantitatively oxidized when twice passed over 3.5 cc. of cobalt oxide catalyst at a rate of 20 to 25 cc. per minute and 550° C., followed by flushing at this temperature, provided the ratio of oxygen to methane was at least 3 to 1.

Comparisons made between the slow-combustion and catalytic oxidation methods show complete agreement at all concentrations of methane.

Two procedures are given for the use of this catalyst: the utilization of a single furnace with a compound combustion tube, and the use of two furnaces employing separate combustion tubes with a modified manifold. The authors recommend the latter.

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Molecular Weight of Cracked Distillates

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The results of a series of determinations, by the cryoscopic method, of the molecular weights of various cracked stocks, all from Midcontinent gas oil, and of a few Midcontinent pressure-still charging stocks are given. Some novelties in the cryoscopic determination are presented. The molecular weight results are correlated with boiling point, viscosity, and density to simplify the estimation of the molecular weight of any given cracked stock.

MOLECULAR weights are an important property of petroleum products, finding extensive use in the design of refinery equipment. However, the routine determination of molecular weights is not practicable, because of the care and time required in this type of work. Some means of estimating molecular weights from other more easily determined properties is therefore desirable. For straight-run stocks this need was met by a previous study (*3*), and in this paper the results of an extension of this work to cracked stocks are given. Some modifications have also been made in the method of making the determination.

Preparation of Samples

The cracked stocks used in this work were all prepared in pilot-plant cracking equipment. One set of samples was prepared in this plant from a Midcontinent gas oil by simulating conditions of a commercial liquid-phase process in which the product boiling above naphtha end point and below a heavy tar is recycled. A product of 450° F. (232° C.) end point on the A. S. T. M. distillation was produced. The distillate and cycle stocks were cut into 5 per cent cuts in a Hempel-type column and the samples thus obtained were studied. (These samples are numbered from 200 up in the tables and data which follow.)

Another set of samples was obtained by the successive once-through vapor-phase cracking of a Midcontinent gas oil. In this process no stock was recycled with the fresh feed, but the product from the first once-through cracking was fractionated to eliminate gasoline and heavy tar, and the residue was fed through the still in a separate operation. This was repeated five times. Selected cuts of the various cycle stocks were chosen for study.

Certain Midcontinent straight-run cuts were also examined.

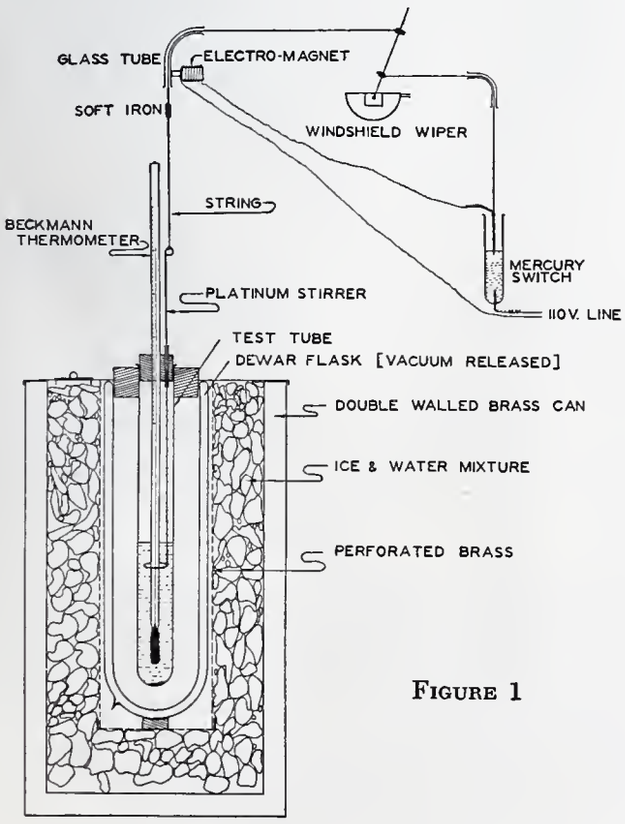

Figure 1

Apparatus and Procedure

Molecular Weights. The apparatus used is illustrated in Figure 1, which will require little explanation. Attention is called to the stirring device which lifts the stirrer slowly and after a pause drops it suddenly, thereby producing the maximum of agitation with a minimum and uniform heat development in the solution. It also prevents the mercury thread from sticking and reduces supercooling of the solution. The Dewar flask with vacuum released was found to give the right amount of cooling of the solution for convenient reading when the temperature difference between the bath and solution was 4° to 5° C. (7.2° to 9° F.). The same results have been obtained by other investigators by maintaining a smaller temperature differential between the bath and solution, but for accurate determinations this requires means for varying the bath temperature in order to keep the temperature difference constant.

In making a determination, the solvent was measured out with a pipet, the temperature being noted. Two grams

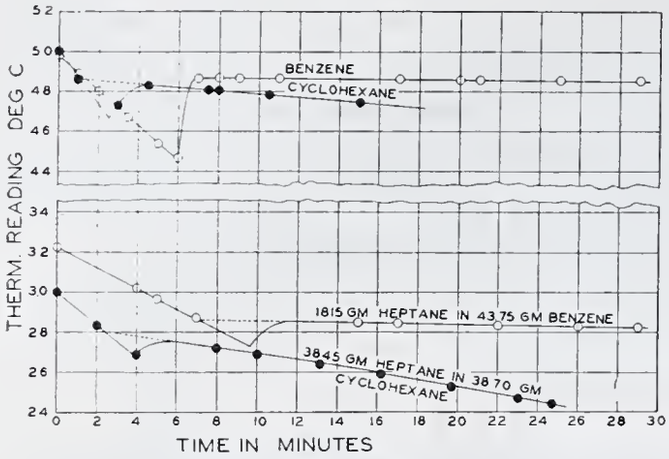

FIGURE 2

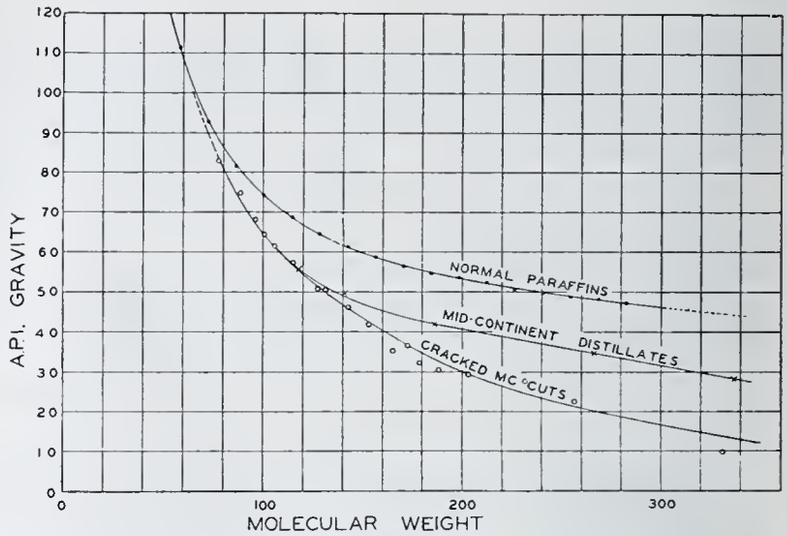

FIGURE 3

of pulverized barium perchlorate were added, this drying agent having been found more satisfactory than sodium sulfate. The thermometer and stirrer were placed in the solution and the whole immersed in an ice bath and stirred until crystals appeared, then removed and warmed in the hand until they melted. This was repeated once or twice more. This precaution, which is due to Gullick (*4*), improves the constancy of the freezing points. The whole apparatus was then put together, the stirrer started, and readings were made of the thermometer at regular intervals. When a steady state had been reached after crystals had formed, a cooling curve was plotted and the freezing point determined as described by Steed (*6*).

The freezing point of the solvent having been obtained, the weighed solute was added in a sealed thin-walled glass bulb, and broken by the stirrer and the freezing point determination was repeated.

In a number of cases the freezing points corresponding to three or more different concentrations of solute were determined, and the apparent molecular weight determined by the formula

$$M = \frac{(F - d)W}{dS} \tag{1}$$

obtained by rearranging the usual equation

$$d = F \frac{\frac{W}{M}}{S + \frac{W}{M}} \tag{2}$$

where M = apparent molecular weight
F = cryoscopic constant of the solvent
d = freezing point depression in ° C.
W = weight of solute added
S = moles of solvent

Since widely varying values of the cryoscopic constant were found in the literature, F was calculated by the equation

$$F = -\frac{R\Theta^2}{\Delta H_\Theta} \tag{3}$$

from recent data of Parks and Huffman (*5*)

where R = gas constant
Θ = freezing point of solvent, degrees Kelvin
ΔH_Θ = heat of solidification of the solvent at the freezing point

The values of F used for the three solvents were

Benzene	65.60
Cyclohexane	248.9
Nitrobenzene	55.78

When computed in this way, the apparent molecular weight tends to increase with increasing concentration, and the exact value is found by plotting the concentration against apparent molecular weight and extrapolating to zero concentration.

In an attempt to avoid determinations at more than one concentration, a study was made of the cryoscopic constant F. The values used for Θ and ΔH_Θ in Equation 3 to obtain the cryoscopic constants given apply to the solvent, and hence Equation 1 is exact only at infinite dilution. No satisfactory method of obtaining ΔH_Θ at other than infinite dilution was found. However, it was found that the equation

$$M = \frac{(F - 2d)W}{dS} \tag{4}$$

gave extremely constant values for the molecular weight, regardless of the concentration, and these values were identical with those obtained by the extrapolation method of Wilson

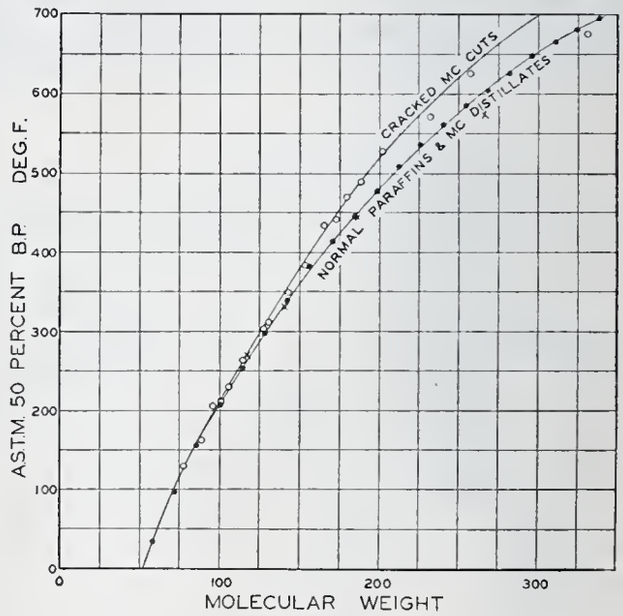

FIGURE 4

and Wylde (*7*). A study of the thermodynamics has disclosed no theoretical basis for this equation, and since in the case of nitrobenzene Equation 4 produces only about half the required correction over Equation 1, this method is advanced as empirical only and to be used only on benzene and cyclohexane at present. Since there might be some question about the results obtained, the samples for which only a single determination was made are indicated in Table II.

The nature of the results obtained with the second formula

is illustrated in Table I by some determinations of the molecular weight of pure cyclohexane and sample 225.

Table I. Results with Equation 2

Sample	Weight of Sample	Depression	Molecular Weight by Equation 4
	Grams	*° C.*	
Cyclohexane in 0.5582 moles of benzene	0.5073	0.694	84.09
	0.7930	1.072	84.10
	1.1283	1.505	84.07
	1.446	1.907	83.93
		Av.	84.05
		Actual	84.10
Sample 225 in 0.5632 moles of benzene	0.5571	0.416	154.0
	0.9081	0.679	152.6
	1.4121	1.040	153.1
	2.2448	1.628	152.6
	2.8428	2.036	152.5
	3.5376	2.487	153.1
		Av.	153.0

In selecting a solvent, benzene was used in the majority of the determinations, but nitrobenzene was used for light cuts which might possibly contain benzene or cyclohexane. Cyclohexane was used chiefly on samples which contained wax, which has a low solubility in benzene. The two determinations on paraffin distillate, sample 308 in Table II, illustrate the error that may be introduced if wax crystallizes out of the solution. Because of its high cryoscopic constant, cyclohexane has found a good deal of favor for this type of work; observations made during the course of this work, however, indicate that the low latent heat of fusion which produces this high constant gives a steep and somewhat curved time-temperature curve after freezing has started, so that it is hard to determine the exact freezing point with precision. This is shown in Figure 2 where the moles of solvent in the case of benzene and cyclohexane are about the same. Benzene was found on the whole to be more satisfactory.

Other Physical Properties. Viscosities were determined on a set of three modified Ostwald viscometers, constructed in accordance with the specifications of the British Engineering Standards Association (*1*) and calibrated at 100° and 210° F. (37.78° and 98.89° C.) with a series of eight oils standardized by the Bureau of Standards. Temperatures of 100° and 210° F. were maintained within limits of 0.1° F. by immersion under reduced pressure in vapor baths of carbon disulfide and water, respectively. Check determinations were possible to 1 part in 1000, but the uncertainty in the absolute value of the viscosity of even standard substances is several times this.

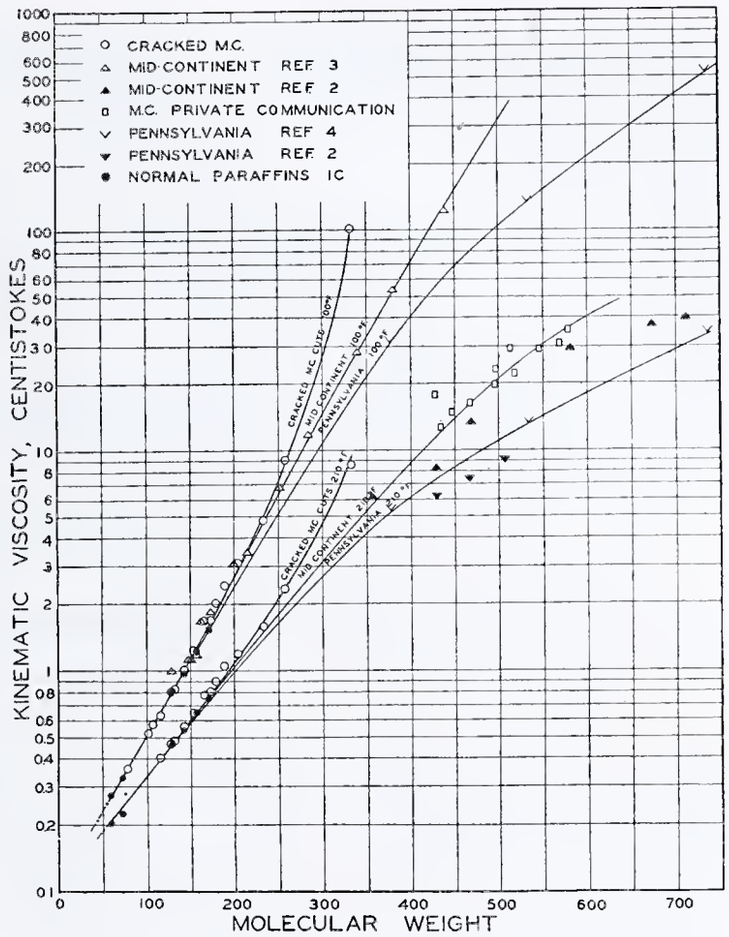

Figure 5

Densities were obtained with precision float hydrometers which were checked against a dilatometer. The accuracy is probably of the order of 5 parts in 10,000.

In the A. S. T. M. distillation corrections were made for barometer and loss.

Results

The results of the actual determinations are summarized in Table II. The relationships between molecular weight and other properties are given in Figures 3 to 5.

Table II. Summary of Experimental Results

Sample No.	Description of Cut	Mol. Wt.	Solvent	Sp. Gr. at 60°/60° F. (15.56°/15.56° C.)	° A. P. I.	50% A. S. T. M.	Kinematic Viscosity in Centistokes 100° F. (37.78° C.)	210° F. (98.89° C.
212	Cut of pressure distillate	77.6[a]	Benzene	0.6599	82.94	129	0.359	...
213	Cut of pressure distillate	88.5[a]	Nitrobenzene	0.6860	74.77	162	...	...
215	Cut of pressure distillate	100.5[a]	Nitrobenzene	0.7223	64.40	212	0.522	...
216	Cut of pressure distillate	105.8[a]	Benzene	0.7334	61.42	230	0.570	...
218	Cut of pressure distillate	114.9[a]	Benzene	0.7501	57.15	264	0.658	0.402
221	Cut of pressure distillate	131.2[a]	Benzene	0.7767	50.67	312	0.829	0.481
223	Cut of pressure distillate	142.5[a]	Benzene	0.7967	46.08	349	1.012	0.459
225	Cut of pressure distillate	153.0[a]	Benzene	0.8161	41.89	383	1.237	0.647
228	Cut of pressure distillate	172.5[a]	Benzene	0.8421	36.54	442	17.00	0.803
231	Cut of cycle stock	96.0[a]	Nitrobenzene	0.7090	68.08	206	...	...
232	Cut of cycle stock	127.3[a]	Benzene	0.7759	50.87	303	0.803	0.467
235	Cut of cycle stock	165.1	Benzene	0.8483	35.30	434	1.690	0.779
238	Cut of cycle stock	178.8	Benzene	0.8638	32.32	470	2.025	0.897
242	Cut of cycle stock	188.3	Benzene	0.8736	30.48	489	2.43	1.054
246	Cut of cycle stock	203.3	Benzene	0.8799	29.33	528	3.08	1.199
249	Cut of cycle stock	232.2	Benzene	0.8888	27.70	571	4.78	1.581
250	Cut of cycle stock	257.2[a]	Benzene	0.9191	22.45	626	9.08	2.352
251	Pressure tar	330.9	Benzene	1.013	9.7	676	101.7	8.58
300	Gas oil charge for once-through runs	266.0	Benzene	0.8510	34.77	586	5.65	1.728
305	Virgin Midcontinent naphtha cut	141.0	Benzene	0.7805	49.80	330	0.922	...
306	Virgin Midcontinent naphtha cut	117.8	Benzene	0.7557	55.74	270	0.692	...
307	Kerosene cut	186.6	Benzene	0.8162	41.87	444	1.85	0.856
308	Paraffin distillate	336.8	Cyclohexane	0.8868	28.07	722	23.7	4.26
308	Paraffin distillate	370.1	Benzene	....	...	...	...	...
309	Virgin Midcontinent gas oil	265.6	Benzene	0.8516	34.66	574	5.59	...
310	Once-through cycle stock	241.2	Benzene	0.8584	33.34	564	4.78	1.523
315	Cut from No. 310	223.8	Benzene	0.8518	34.62	529	3.49	...
330	3 Times-through cycle stock	221.6	Benzene	0.8845	28.45	546	4.14	1.371
350	5 Times-through cycle stock	205.3	Benzene	0.9073	24.29	531	3.74	1.276
355	Cut from No. 350	193.0	Benzene	0.8915	27.21	501	2.77	...

[a] Several determinations made with extrapolation to zero concentration. Only one determination in all other cases.

Figure 3 shows a plot of A. P. I. gravity versus molecular weight for the normal paraffins and for Midcontinent straight-run and cracked stocks. The line for straight-run stocks differs slightly from that previously presented. This difference is due to a slight difference in the Midcontinent pipe-line crude, and not to a change in procedure, as was shown by checking some of the old samples.

Figure 4 is a similar plot of molecular weight against 50 per cent A. S. T. M. boiling point (760 mm.). Since there is no stem correction in the A. S. T. M. method, the 50 per cent point shown by pure substances of various boiling points was actually determined, and a correction plot prepared so that the 50 per cent boiling point which would be shown by each pure hydrocarbon could be computed. These computed values, not the true boiling points, are used in Figure 4.

Figure 5 is a plot of the kinematic viscosity versus molecular weight. In this plot the results of various determinations in the literature, as well as some other unpublished work, have been incorporated, in the hope of correlating viscosity, viscosity index, and molecular weight for the heavier fractions. The data are somewhat conflicting, and the lines as drawn are, at the upper end, to be regarded as only a first attempt to obtain the desired result.

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Colorimetric Determination of Small Quantities of Chlorides in Waters

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The method generally adopted for the estimation of the chlorides in water has consisted of titrating a known quantity of water with a standard solution of silver nitrate, using potassium chromate as the indicator, and calculating the chloride content in parts per million or a similar denomination (*1*). The chlorides in most rain waters and many ground waters are present in too small a quantity to be determined accurately by this method.

A study of over two hundred articles on the composition of rain water in different parts of the world made by Riffenburg (*5*) in 1923 showed the chloride content to vary from a trace to over 50 parts per million, with the average about 3.0 parts per million. Some authors used a 0.1 *N* or weaker solution of silver nitrate to titrate the chlorides, and many did not discuss the method used. Such a variable chloride content indicates that either the method used or the analysis is faulty, and this is confirmed by determination of chloride content in lakes, rivers, and many ground waters. Jackson's chloride maps (*4*) show that some natural waters in the northeastern part of the United States contain as little as 0.2 p. p. m. Lake Superior water showed 1.1 p. p. m. and sixteen rivers in the United States showed less than 2.0 p. p. m. of chlorides (*3*). Twenty-three samples of rain water collected in Washington, D. C., in 1923–1924 and analyzed by Riffenburg (*5*) contained a maximum of 3.0 p. p. m. and an average of about 1.3 p. p. m. Samples collected in central and upper Michigan and Blacksburg, Va., averaged about the same. Williams' (*2*) analyses of rain waters collected in ten different places in the United States showed averages from 1.4 to 0.25 p. p. m. Williams evaporated a larger quantity down to 25 cc. and titrated it with a silver nitrate solution, 1 cc. of which is equivalent to 0.5 mg. of chloride. These analyses show the importance of developing a method that will more accurately estimate very small quantities of chlorides in waters.

An attempt was made to increase the accuracy of the titration by using dilute solutions and greater or smaller volumes of water, but this failed until a modified colorimetric method was used.

The colorimetric modification consists of filling one, or preferably two, Nessler tubes to the mark with the sample to be tested, adding 1 ml. of potassium chromate prepared as in (*1*), and mixing well. One tube is used as the control and to the other is added the silver nitrate solution until the usual red color can be detected in the sample when compared to the control tube. The silver nitrate should be added drop by drop, shaking the tube well, and comparing it with the control after each drop. The silver nitrate used contained an equivalent of 0.05 mg. of chloride per cubic centimeter; it should not be stronger than this and should not be too weak.

Test tubes may be used, but Nessler tubes have been found more satisfactory, since they have polished bottoms and present a longer column of liquid through which to view the color change. Sharper color changes can be produced by allowing the sun to shine on a piece of white paper or white porcelain under the tubes and protecting the tube from the light. Distilled water may be used as the control if the quantity of sample is not sufficient to fill two tubes, and the same control may be used for a number of samples if none shows a different shade of the chromate color. If a different shade of color appears, the sample itself will have to be used as the control.

The burets and pipets used in these analyses were certified by the U. S. Bureau of Standards and the other volumetric apparatus used was calibrated.

Fairly close checks were obtained by evaporating 500 ml. to 50 ml. and titrating by the usual method, using a yellow light to increase the sharpness in the end point.

Analyses of twenty samples of rain water collected at Blacksburg, Va., during the past year and a half show a maximum of 0 4 p. p. m., a minimum of 0.05 p. p. m., and an average of 0.23 p. p. m.

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Determination of Minute Amounts of Copper in Milk

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The variations in the copper content of milk as reported by different investigators show the need for a critical study of the methods used. A consideration of colorimetric methods has shown that the sodium diethyldithiocarbamate method is the most suitable for the estimation of small amounts of copper. The metal is first separated either by hydrogen sulfide or by microelectrolysis. It is essential to eliminate all sources of contamination. It appears particularly advantageous to substitute centrifugalization for filtration.

The proposed colorimetric method has been thoroughly checked, both with copper sulfate solution and milk ash solution, by experiments in which the copper deposited by electrolysis both before and after separation with hydrogen sulfide was determined first by weighing on the microbalance and then colorimetrically. A number of samples of milk and milk products have been analyzed by the hydrogen sulfide–carbamate method.

IN RECENT years considerable interest has been shown in the copper content of cow's milk, partly because small amounts of copper in foods may have a beneficial effect in preventing or curing anemia and partly because the copper may have a decidedly unfavorable effect in catalyzing oxidation reactions which destroy vitamins and enzymes and cause undesirable flavors.

As may be expected, the copper content of milk will vary considerably according to the treatment it receives after milking. However, variations in the copper content of uncontaminated raw milk obtained directly from the cow, as judged by the results of different investigators, seem too great to be accounted for merely by the difference in season or locality, particularly as Elvehjem, Hart, and Steenbock (*14*) have shown that the copper content of milk does not vary with locality or with the copper content of the feed.

The results of fourteen investigations are given in Table I. Earlier workers found values ranging from 0.20 to 0.80 part per million of copper in uncontaminated raw milk, while more recent workers found values ranging from 0.06 to 0.20 p. p. m. This difference is doubtless due very largely to the gradual improvements in technic of analysis and sampling, and it is believed that the more recent results are far more reliable than the earlier ones. It is probable that the widely quoted results of Supplee and Bellis (*41*) are far too high and that much of the controversy concerning the role of copper in curing nutritional anemia, referred to by Keil and Nelson (*24*), could have been avoided if one reliable method of copper analysis had been adhered to by all the investigators.

The purpose of the present investigation was to make a critical examination of the available methods in order to select a method which would be suitable for comparatively accurate and rapid determination of the minute amounts of copper in pure uncontaminated dairy products.

SUMMARY OF NONCOLORIMETRIC METHODS

Yoe (*49*) and Pope (*30*) give comprehensive bibliographies on the determination of copper in foods. The usual gravimetric methods of copper analysis—the direct weighing of the copper sulfide precipitate or the direct weighing on the regular analytical balance of the copper deposited by electrolysis—are, of course, not suitable for the estimation of such minute amounts of copper as are found in raw milk.

Lampitt and co-workers (*26*) made a survey of the methods for determining minute amounts of copper in foods and finally

TABLE I. COPPER CONTENT OF MILK AS REPORTED BY VARIOUS INVESTIGATORS

Investigator	Year	Source and Treatment of Milk	Copper	No. of Samples	Method of Separation	Method of Analysis
			P. p. m.			
Supplee and Bellis (*41*)	1922	Raw, uncontaminated	0.20–0.80 (0.521)[a]	23	NH_4OH	Xanthate
King and Etzel (*25*)	1927	Raw	(0.43)[a]	5	NH_4OH	Xanthate
Quam and Hellwig (*33*)	1928	Raw, uncontaminated	0.26–0.52	14[b]	NH_4OH	Xanthate
		Pasteurized	0.60–1.60	6		
Elvehjem and Lindow (*15*)	1928	Raw	0.132, 0.163, 0.126	3	H_2S	Biazzo
Elvehjem et al. (*14*)	1929	Raw, collected in glass	0.123–0.184 (0.147)[a]	[c]	H_2S	Biazzo
Grendel (*19*)	1930	Raw	0.09–0.14 (0.12)[a]	7	Microelectrolytic	Carbamate
		Pasteurized	0.16–0.29 (0.22)[a]	12		
Guthrie et al. (*20*)	1931	Raw, in contact with tin only	0.62, 0.55, 0.54	3		Xanthate
		Raw, commercial sample	0.50, 0.50, 0.30	3		
		Pasteurized, commercial sample (same)	0.62, 0.66, 0.55	3		
Keil and Nelson (*24*)	1931	Raw, collected in glass	0.24	1		Carbamate
Ansbacher et al. (*3*)	1931	Dried (Klim)	1.2–2.0		H_2S	Chromotropic
Davies (*11*)	1931	Raw, in contact with heavily tinned pails	0.15–0.65	15	NH_4OH	Xanthate
		Raw, commercial samples	0.20–1.40	22		
		Pasteurized	0.40–4.0	39		
		Dried	2.8–4.6	2		
Zondek and Bondmann (*52*)	1931	Raw	0.15–0.20	90		Warburg (*46*)
McFarlane (*27*)	1932	Raw, uncontaminated	0.096, 0.068, 0.075	3	H_2S	Carbamate
Remy (*36*)	1932	Raw, freshly milked	0.16, 0.13			Biazzo
		Raw, children's milk	0.11			
		Pasteurized	0.12			
		Condensed, unsweetened	0.45			
		Dry skim	0.83			
Present work	1934	Raw, uncontaminated	0.051–0.132 (0.077)[a]	18	H_2S	Carbamate
		Pasteurized	0.088–0.741 (0.253)[a]	7		
		Dried	1.37–17.15	5		
		Buttermilk	0.549	1		

[a] The average values of copper content are given in parentheses. [b] Samples from 4 states. [c] Samples from 13 states.

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developed a method of their own, using quinisol to precipitate the copper. If manganese were present, it would also be precipitated and the two could be separated by redissolving the precipitate and determining the copper electrolytically. The amount of copper determined by this method was usually from 1 to 10 mg.

The volumetric iodide method recommended in Standard Methods of Food Analysis of the Association of Official Agricultural Chemists was revised by Walker (*44*) and the revision adopted as the tentative method of the association (*4*). Collaborative work carried out by various laboratories from time to time (*28, 29, 45*) on samples submitted by the association showed that while the method was satisfactory for determining quantities of copper approximating 2 mg., a supplementary colorimetric method was desirable in determining smaller amounts of copper.

None of the above methods is sufficiently sensitive for the analysis of uncontaminated milk.

Traces of copper were found in milk by spectrographic examination of the milk ash by Wright and Papish (*48*), by Zbinden (*50*), and by Blumberg and Rask (*7*). At present such methods do not permit a sufficiently accurate quantitative estimation.

The magneto-optic nicol rotation method for quantitative determination of small amounts of copper has been investigated by Bishop, Otto, and Baisden (*6*). No preliminary separation of the copper is required and concentrations of the metal between 5×10^{-12} and 1×10^{-4} grams of copper per cubic centimeter may be accurately determined. A calibration curve of nicol rotation against copper concentration must be made. This would seem to be an excellent method for determining very small amounts of copper, but it is tedious and requires much time and great skill on the part of the analyst.

The catalytic effect of copper on the decomposition of hydrogen peroxide and measurement of the volume of gas evolved were used by Quartaroli (*34*) to estimate small amounts of the metal in biological materials. The method is said to be sensitive to 0.1 p. p. m.

The catalytic effect of copper in the oxidation of cysteine to cystine and the subsequent measurement of the oxygen evolved in a given time was used by Warburg (*46*) for copper determinations in blood, and was applied to milk by Zondek and Bondmann (*52*). The method was sensitive to 0.00001 mg. of copper and consequently permitted the use of exceedingly small samples of milk, 0.1 to 0.3 cc. However, there was always a comparatively very large and variable reading on blank controls. Andresen and Nielsen (*2*) attribute such variations to the possible formation of hydrogen peroxide during the oxidation, the hydrogen peroxide then decomposing in variable degrees depending upon the pH of the medium. Using the method with known amounts of copper, they found errors of 24.9 per cent at pH 6.66, 55.6 to 58.8 per cent at pH 7.64, and 78.6 per cent at pH 8. They found no proportionality between oxygen absorption and the amount of cysteine or the concentration of copper.

A Critical Study of Colorimetric Methods

A tabulation of colorimetric methods for the determination of copper is presented in Table II. Only Nos. 9, 10, and 11 have been commonly used and along with the chromotropic titrimetric method (No. 15) were investigated experimentally by the authors.

Potassium Ethyl Xanthate Method. This test is usually carried out upon 100-cc. solutions, but its sensitivity may be increased if the volume of solution is decreased. The yellow color developed is compared with a set of standards containing varying amounts of copper.

A study was made of the sensitivity of the test when carried out with 2.5 cc. of 0.1 per cent xanthate reagent in 25-cc. solutions at a pH of 6.9. The test was most accurate when applied to solutions containing from 0.005 to 0.018 mg. of copper, the error being 10 to 15 per cent in this range. Below this range the error increased gradually, being as much as 50 per cent in solutions containing 0.001 to 0.002 mg. of copper. The error increased to 20 per cent with larger amounts of copper and, if there was more than 0.028 mg. of copper, the turbidity interfered with an accurate comparison of the color. For this reason aliquot portions should be used for comparison when samples contain more than 0.018 mg. of copper.

The main objection to the xanthate method is the development of turbidity which interferes with the color comparison if the pH is not carefully controlled. Scott (*39*) stated that the test must be carried out in neutral or very slightly acid solution. Lampitt and co-workers (*26*) found that on either side of neutrality an opalescence was produced which they said was due to a precipitate of copper xanthate or possibly sulfur. Drabkin and Waggoner (*12*), on the other hand, stated that adjustment of the reaction to pH 3.8 was important, as the maximum color was developed at that point. In some tests conducted in this laboratory the pH value of several standard copper solutions was varied by the use of phosphate or phthalate buffers in the acid range and by borate–potassium chloride buffers in the more alkaline range. The results showed that for a copper concentration of 0.02 mg. in 25 cc. of solution it was best to use a pH from 7 to 8.5 and that turbidity would occur in due time above and below this range. In the presence of higher amounts of copper, such as 5 mg., no precipitate was formed at pH 3.0 or 3.5, but increasingly rapid precipitation occurred as the pH was increased from 5.2 to 8.1.

Probably the least interference from turbidity would be encountered at pH 7.0, keeping the copper concentration between 0.005 and 0.020 mg. in 25 cc. of solution. The color comparison should preferably be made within 15 minutes.

Nitrosochromotropic Acid Method. This method was used by Ansbacher, Remington, and Culp (*3*) to determine the copper content of several foods, the advantage claimed being that very small amounts of copper could be determined with great accuracy. Nitrosochromotropic acid forms with copper a purple permanganate-colored compound. The chromotropic acid reagent is standardized with respect to copper, and then added from a microburet for titration of the unknown copper solution.

In one case an accurate estimation of 0.0098 mg. of copper was obtained by this method, but the end point was very difficult to distinguish. When all the copper in the solution had combined with the chromotropic acid, forming the wine-red or permanganate-colored compound, the chromotropic acid subsequently added in the titration underwent no color change, retaining its original brownish red color. However, this was masked to a large extent by the wine-red or permanganate color of the copper compound which still predominated at this point. The immediate change was barely perceptible, the brown color becoming definite only upon adding an excess of the reagent. This method was accordingly not considered satisfactory for the authors' work.

Thiocyanate-Pyridine (Biazzo) Method. This method as used by Elvehjem and Lindow (*15*) was tried out on a standard copper sulfate solution. The green color of the copper-thiocyanate-pyridine complex is extracted and compared in a colorimeter. Very pale green solutions were obtained with 0.01 to 0.05 mg. of copper in the samples, and it was possible to obtain accurate readings only when the copper content of unknown and standard differed by less than 0.01 mg. When the copper content was around 0.1 mg. the colors were much easier to compare.

Sodium Diethyldithiocarbamate Method. The method as given by Callan and Henderson (*8*) was conducted in 100-cc. Nessler tubes using 10 cc. of reagent. As with the xanthate method, the sensitivity could be increased if the volume of solution was decreased. This test was modified by using 1 cc. of 0.1 per cent aqueous sodium diethyldithiocarbamate solution to 10 cc. of the solution to be tested, which contained 2 cc. of 20 per cent ammonium hydroxide. Amounts ranging from 0.001 to 0.0055 mg. of copper could be readily determined by this method with an accuracy of 0.0002 mg. The color was a clear yellow, varying in intensity with the amount of copper present. Callan and Henderson stated that the color was the same in acid, neutral, or alkaline solutions, but recommended making the solution slightly ammoniacal. With the amounts of copper used the addition of 1 or 2 cc. of 20 per cent ammonia produced colors that were clearer, sharper, and more easily compared. Without the ammonia the colors tended toward a dull straw tint. McFarlane (*27*), using this test for the determination of copper in biological material, stated that the use of nitric acid for oxidizing the copper sulfide was less desirable than a bromine–sulfuric acid mixture, in that it decreased sensitivity. The authors found, however, that the use of nitric acid did not interfere in any way with the color developed if the solution were made ammoniacal before adding the reagent.

Callan and Henderson found that most metals, with the exception of calcium and magnesium, interfered with the test by producing turbidity. However, interference from other metals is not encountered when the copper content lies between 0.001 and 0.005 mg., if the metal is first separated from the other milk ash constituents, and if centrifugalizing is used after the addition of excess ammonium hydroxide to eliminate the slight turbidity which usually occurs at that step.

McFarlane (*27*) extracted the color with amyl alcohol and made comparisons with a standard in a colorimeter. Thatcher (*42*) found that the use of isoamyl instead of normal amyl alcohol gave a much better separation of the liquids. Williams (*47*) extracted the color with chloroform. Haddock and Evers (*21*) extracted with carbon tetrachloride and determined the intensity of the yellow color in a Lovibond tintometer, using a curve previously determined for known amounts of copper, in order to transform the readings to milligrams of copper. They used this method for determining 0.008 to 0.088 mg. of copper with a maximum error

Table II. Colorimetric Methods for Determination of Copper in Minute Amounts

No.	Reagents Used	Color	Limit of Sensitivity	Remarks	Reference
			P. p. m.		
1	Sodium arsenite (anhydrous $AsCl_3$ in NaOH)	Green	8		Currie (*10*)
2	Excess NH_4OH	Blue	5		Scott (*39*)
3	Alcoholic solution of benzidine in presence of KCNS	Blue	1		Fleming (*17*)
4	Alcoholic solution of guaiacum resin	Blue	0.5		Fleming (*17*)
5	Potassium ferrocyanide	Purple to brown	0.4		Scott (*39*)
6	Piperidinium piperidyldithioformate in alcoholic solution	Yellowish brown	0.2		Harry (*22*)
7	Direct green B	Reddish violet	0.1	Particularly suitable for determination of Cu in distilled water	Sisley and David (*40*)
8	Dimethylglyoxime in presence of ammonium persulfate as oxidizing agent	Intense permanganate	0.1		Clarke and Jones (*9*)
9	Potassium ethyl xanthate[a]	Yellow	0.1	Greatest accuracy, 1 to 2 p. p. m. of Cu	Supplee and Bellis (*41*)
10	Potassium thiocyanate and pyridine[a]	Green	0.02 mg.	Color extracted in $CHCl_3$	Biazzo (*5*), Elvehjem and Lindow (*15*)
11	Sodium diethyldithiocarbamate[a]	Golden brown	0.01		Callan and Henderson (*8*)
12	2 per cent phenolphthalein in 20 per cent KOH decolorized by zinc dust (Kastle-Meyer reagent) and few drops of H_2O_2	Pink	0.01		Thomas and Carpentier (*43*)
			Mg.		
13	Dithioöxamide $(CS{\cdot}NH_2)_2$	Olive-green	0.01	Suitable for materials high in iron	Allport and Skrimshire (*1*)
14	Diphenylthiocarbazone (dithizone) in CCl	Yellow-brown in neutral or slightly alkaline soln., purple in slightly acid soln.	0.004	Suitable for determining traces of Cu in other metals or metal oxides	Fischer and Leopoldi (*16*)
15	Nitrosochromotropic acid	Permanganate	0.002	Titration method	Ansbacher et al. (*3*)
16	0.2 per cent soln. of cryogenin, incubation at 40° C. for 40 min.	Red	0.0005		Sarata (*37*)

[a] These methods have been most used for determination of copper in milk.

of 0.003 mg. With pale-colored solutions, however, the authors prefer to match the colors with a series of standards in aqueous solution.

Summarizing experience with these four methods, the chromotropic acid method can be eliminated because of the difficulty in distinguishing the end point. The Biazzo method is not sufficiently sensitive. The possibility of interference due to turbidity makes the xanthate method undesirable. The carbamate method appears to be by far the most desirable, since it is the most sensitive and the disturbing factor of turbidity is not encountered.

Separation of Copper from Other Ash Constituents

The constituents of the milk ash causing the most interference with the colorimetric copper determination are calcium phosphate and iron. Commonly copper is separated from interfering elements by ammonium hydroxide, hydrogen sulfide, or electrolysis.

Interference of Iron. Iron, if present, will interfere with the colorimetric estimation of copper, whether carried out by the carbamate, xanthate, or Biazzo methods. Haddock and Evers (*21*) stated that by adding citric acid and ammonia to the solution containing the iron in the ferric condition, quantities of copper as low as 0.005 mg. could be accurately determined in the presence of 0.25 gram of iron. The carbamate reagent was added without previous separation of the iron, and the copper-carbamate compound extracted with carbon tetrachloride. The presence of as much as 0.3 gram of calcium phosphate did not interfere. They stated that the pH should be approximately 9.0 and should not exceed this value, as precipitation will occur. Drabkin and Waggoner (*12*) found that the addition of a small amount of sodium pyrophosphate would eliminate the interference due to iron, as iron pyrophosphate did not react with the xanthate or Biazzo reagents unless more than 0.2 mg. of it was present in the sample. Elvehjem and Hart (*13*), however, found that the use of pyrophosphate might lead to a serious loss of copper unless the temperature and pH were carefully controlled. They also stated that in determining copper in biological materials there will be no interference due to iron unless it is present in excess of the phosphate, and that in analyzing one hundred food materials by the Biazzo method this difficulty was encountered in only a few cases.

For determining small amounts of the copper in pharmaceutical preparations high in iron, a method has more recently been developed by Allport and Skrimshire (*1*). After wet oxidation of the organic matter, the solution is made ammoniacal and the copper extracted with diphenylthiocarbazone in chloroform. The extracted copper is then estimated colorimetrically with dithioöxamide. The authors advocate this method also for determining copper in ferruginous diets and foodstuffs.

Ammonia Method. The precipitation of insoluble phosphates and hydroxides with excess ammonia, leaving copper in solution, has been used by Supplee and Bellis (*41*) and others for the separation of copper from the other constituents of milk ash. Most investigators have assumed that a double ammonia precipitation frees the phosphate precipitate from copper. Ansbacher et al. (*3*) and McFarlane (*27*) have questioned the complete recovery of copper by this method, as the voluminous precipitate of calcium phosphate tends to occlude some of the copper unless a number of precipitations are carried out. Ansbacher and co-workers recovered 5 per cent of the copper from the second ammonia precipitate.

The method was tested in this laboratory using two samples of milk to which had been added, respectively, 0.425 and 0.215 p. p. m. of copper. Two hundred cubic centimeters of milk were ashed, the ash was dissolved in hydrochloric acid, and the phosphates were precipitated by adding excess ammonium hydroxide. The solution was centrifugalized, and the precipitate redissolved in hydrochloric acid, reprecipitated with ammonium hydroxide, and again centrifugalized. The solution was poured off, combined with that from the first centrifugalization, and evaporated to a small volume, and copper determined by the carbamate method, 73 per cent of the added copper being recovered in both cases. The sample containing 0.215 p. p. m. was subjected to a third and fourth ammonia precipitation with further recovery of 12 and 10 per cent of the total copper present. Thus a total of 95 per cent of the total added copper was recovered with four ammonia precipitations. From a sample containing 0.846 p. p. m. of added copper and subjected to three ammonia precipitations, 77 per cent of the added copper was recovered.

These results indicate that this method of separating the copper is not accurate unless at least four precipitations are carried out, such a procedure making necessary the time-consuming evaporation of large amounts of solution.

Hydrogen Sulfide Method. Supplee and Bellis (*41*) and Walker (*44*) have stated, without giving experimental proof, that the precipitation of copper with hydrogen sulfide was doubtful for small amounts of copper. Drabkin and Waggoner (*12*) found that 0.01 mg. of added copper in milk was not recovered and that 0.05 mg. was recovered to the extent of 60 per cent with the hydrogen sulfide method. Elvehjem and Hart (*13*), however, have criticized their technic.

On the other hand, Elvehjem and Lindow (*15*) recovered 92 to 98 per cent of added copper from milk, and Ansbacher et al. (*3*) obtained quantitative precipitation of copper sulfide from samples of standard copper solutions containing 0.049 mg. of copper. Gebhardt and Sommer (*18*) recovered 89.6 to 113.6 per cent of added copper in milk samples containing 0.0758 to 0.2062 mg. of copper. McFarlane (*27*) obtained quantitative precipitation of copper from copper sulfate solutions by hydrogen sulfide when the acidity and volume of solution were controlled.

The solubility product of copper sulfide is 8.5×10^{-45}. Theoretically then, only negligible quantities of copper would be left in solution after precipitation of the sulfide. Experiments on the comparative solubility of copper sulfide in water and in 1 per cent hydrochloric acid solution showed that while there was slightly more copper sulfide dissolved in the acid solution, less than 0.01 mg. of copper remained in 1 liter of solution after precipitation of the sulfide.

Various procedures have been recommended for the treatment of the copper sulfide precipitate, most of which involve filtration of the precipitate through asbestos or filter paper. Gebhardt and Sommer (*18*) extracted the precipitate with chloroform, thus eliminating the necessity for filtration. According to the authors' work, this last procedure was more accurate than the filtration methods, which gave high results, indicating that the filter paper might be a source of contamination. Walker (*44*) stated that the digestion of copper sulfide along with filter paper gave high results. Although Elvehjem and Lindow (*15*) recovered 92 to 96 per cent of added copper from a milk sample by the filtration method, the error due to the use of filter paper would not be apparent, as these results were obtained by subtracting the amount of copper found in the sample containing added copper from that found in the control sample. More recently McFarlane (*27*) used sintered glass filters for filtering the copper sulfide precipitate. The following experiments served to demonstrate the importance of this source of contamination, which has been overlooked by most investigators:

Five different brands of filter paper (7 cm. diameter) were ashed and analyzed for copper. The results showed from 0.00167 mg. of copper in a good grade of acid-washed paper to 0.0127 mg. of copper in a relatively poor grade of paper. However, some of the acid-washed papers had a higher copper content than non-acid-washed papers. None of the papers tested were found free from copper. Much of the copper was leached out of the paper by treatment with dilute copper-free hydrochloric acid, the amounts ranging from 0.00137 to 0.0051 mg. in the same series of papers. Williams (*47*) recommended treating the filter paper with copper-free hydrochloric acid for 24 hours, but the authors found that even such a treatment did not free it from interfering amounts of copper.

The following experiments were conducted in order to find out if centrifugalization could be used instead of filtration for separating the copper sulfide precipitate.

Two samples of milk, each 100 cc., containing 0.536 and 1.071 p. p. m. of added copper, respectively, were ashed, dissolved, precipitated, and centrifugalized within 1.25 hours after precipitation with a copper recovery of 96.4 and 93.5 per cent. Later several samples were centrifugalized immediately after precipitation and the supernatant solution was held overnight and recentrifugalized. Various amounts, up to 30 per cent of the total copper present, were recovered upon recentrifugalization. Therefore it seemed safer to allow the samples to stand overnight before centrifugalization in order to permit colloidal sulfide to settle out. This procedure is also followed when the sulfide is separated by filtration. While the present work was in progress it was found that Sarata (*38*) used centrifugalization to separate the copper sulfide precipitate in the determination of copper in blood.

Microelectrolytic Method. The usual macroelectrolytic method has been much used for materials containing large amounts of copper. Redfield, Coolidge, and Shotts (*35*) described an electrolytic method which gave accurate results on samples containing 0.3 to 0.8 mg. of copper. Inouye and Flinn (*23*) used the electrolytic method for separating copper in biological materials, dissolving the deposited copper, adding potassium iodide, and titrating with 0.005 *N* thiosulfate. They stated that the accuracy was 0.02 mg. Pregl (*32*) described a microelectrolytic method for copper which he used for determining copper in canned vegetables, the smallest amount of copper found in the samples tested being about 1 mg.

Zbinden (*51*) recently described a unique electrolytic method. Copper previously deposited on a platinum cathode was caused to dissolve by reversing the current. When solution was complete there was a sharp change of potential. The amount of copper in the sample was then calculated by measuring the current produced by dissolving the copper and noting the time required for complete solution as determined by the sudden change in potential. Twenty-five samples of fresh milk from different countries in Europe were found to contain from 0.50 to 0.85 p. p. m. of copper. The author states, however, that further study is being made of the method to improve the technic.

Grendel (*19*) analyzed a number of milks by a microelectrolytic method using a technic similar to that described by Pregl. The milk ash was dissolved in nitric acid and filtered, and sulfuric acid added and evaporated until the nitric acid was driven off. The residue was dissolved in water acidified with sulfuric acid and filtered. Electrolysis was carried out in a short Jena glass tube fitted with a platinum screen cathode, using 2 volts, 10 to 15 milliamperes at 100° C. for 15 to 20 minutes. The copper was dissolved from the cathode in 1 cc. of 4 *N* nitric acid and estimated by the carbamate method. The results obtained by Grendel on a number of raw milk samples by this method were 0.09 to 0.14 p. p. m., which agree well with the values reported by Elvehjem and co-workers (*14*, *15*) and McFarlane (*27*). Grendel's method was investigated but was discarded because of the troublesome precipitate of calcium sulfate.

It was found that the method of Benedetti-Pichler referred to by Pregl (*32*), in which electrolysis was carried out in nitric acid solution, could be used with success in separating the copper from milk ash. The deposition of other milk ash constituents along with the copper occurs to a smaller extent in nitric acid than in sulfuric acid solution.

In experiments where 0.004 to 0.03 mg. of copper was subjected to electrolysis, the amount of copper left undeposited varied between 0.0012 and 0.0036 mg. and did not increase in proportion to the amount of copper electrolyzed. Therefore in applying this method to the analysis of milk, there should be from 0.02 to 0.05 mg. and certainly not less than 0.01 mg. of copper present.

In the determination of copper in copper sulfate solutions by this method it was found that if the acid concentration was too low the copper was not all deposited. In the analysis of milk, however, the amount of acid necessary to dissolve the ash readily furnished enough excess to insure proper deposition of the copper. Too large an excess of acid should be avoided, since this also prevents quantitative deposition of the copper. The presence of 1 per cent of free nitric acid insures quantitative deposition of the copper and may be

judged by observing the amount of bubbling which takes place at the anode.

Both the hydrogen sulfide and the microelectrolytic methods in conjunction with the colorimetric carbamate method were found to be suitable for accurately determining small amounts of copper in milk.

Methods Finally Adopted

General Precautions. Contamination should be guarded against at every step in the procedure. It is of the utmost importance that samples be taken in absolutely clean bottles which preferably have been rinsed with copper-free water. Metal containers of any type should not be used. Laboratory dust and dust from the muffle furnace should be guarded against. Only chemically pure reagents should be used. The distilled water, hydrochloric acid, and ammonium hydroxide should be redistilled from glass until free from copper. The copper contents of the reagents used in very small quantities, such as the nitric acid, glacial acetic acid, and formaldehyde used to preserve the milk samples, were not found to be contaminating factors. Blank determinations should be run and if the amount of copper found is less than 0.001 mg. it may be disregarded. All glassware should be cleaned with chromic acid cleaning solution before use and then rinsed with copper-free water.

Ashing. According to the copper content, 25 to 200 cc. of milk may be used for analysis. Platinum or quartz crucibles previously extracted with sodium acetate according to Elvehjem, Hart, and Steenbock (*14*) should be used, as the copper contamination from porcelain crucibles may be considerable.

Various wet-ashing methods have been proposed for biological materials high in organic matter and have been recommended for ashing milk, as the dry-ashing method has been thought to give low results due to the volatilization of the copper. Gebhardt and Sommer (*18*), however, found the dry-ashing method reliable if the temperature of the muffle was carefully controlled during the ashing process, a temperature of 510° to 565° C. for 3 to 4 hours sufficing to ash 250 cc. of milk. The recovery of added copper by this procedure was over 90 per cent. As copper might be introduced along with the reagents in the wet-ashing method, it was thought best to adhere to the simpler dry-ashing method, taking the precaution to maintain the proper temperature of the muffle.

The evaporation and preliminary ashing may be done in a drying oven or over a free flame. The addition of 5 drops of glacial acetic acid at the beginning of the evaporation will speed up the process and prevent foaming. It is advisable either to suspend an inclined piece of glass or a large glass funnel at some distance above the crucible, to reduce the possibility of contamination. If evaporating over a free flame, the flame must be lowered to prevent spattering when the sample approaches dryness. After most of the carbon has been burned, the crucible is transferred to a muffle furnace to complete the ashing at dull red heat (not over 565° C.). Two to three hours will usually be sufficient to obtain a clean, whitish gray ash.

Hydrogen Sulfide Method. The ash is dissolved in sufficient 20 per cent hydrochloric acid to obtain good solution (about 2.0 cc. of the acid for a 50-cc. milk sample), washing down the sides of the crucible. The solution is warmed gently, keeping the crucible in constant motion, and transferred to a 15-cc. graduated centrifuge tube with water, keeping the volume down to about 7 cc. The tube is centrifugalized at 1800 r. p. m. for 10 minutes to throw down the small amount of undissolved carbon. In a well-ashed sample the amount of carbon is insignificant and may be discarded after washing and recentrifugalizing with 2 cc. of water. The wash water is added to the original solution in a second centrifuge tube. If the volume occupied by the carbon precipitate exceeds 0.2 to 0.3 cc. it should be re-ashed, dissolved, and added to the first ash solution. It is important that the tubes be very carefully cleaned with cleaning solution between each operation, because this greatly facilitates the draining of the tubes when transferring the liquids from one tube to another. Ammonium hydroxide (20 per cent) is added drop by drop until a slight permanent precipitate of calcium phosphate is formed; then sufficient hydrochloric acid to bring the acid concentration to 1 per cent (0.5 cc. of 20 per cent hydrochloric acid per 10 cc. of solution). The volume is brought to 10 cc. with distilled water, or, if over 12 cc., evaporated.

The sample is heated in a beaker of boiling water and saturated while cooling with washed hydrogen sulfide for 15 minutes. The gas should be turned on before the delivery tube is put into the solution and turned off after the tube is removed from the solution to prevent possible loss of the solution on the inside of the tube. During the last 5 minutes the centrifuge tube is placed in a beaker of cold water. A hydrogen sulfide tank is superior to a laboratory generator for the production of the gas, as a steady stream of 100 per cent hydrogen sulfide may be counted upon at all times. A bottle containing copper-free distilled water should be inserted in the line for washing the gas. A bend in the end of the tube leading to the wash bottle prevents possible contamination from the rubber tubing which connects the delivery tube to the glass tube leading from the wash bottle. When saturation has been completed, the delivery tube should be rinsed with 0.5 to 1.0 cc. of freshly prepared hydrogen sulfide water (containing 1 per cent hydrochloric acid) as it is removed from the solution. It is advisable to use a clean delivery tube for each sample. The centrifuge tube is immediately stoppered and allowed to stand overnight. Corks should be soaked in 20 per cent hydrochloric acid for 15 minutes, rinsed with copper-free distilled water, and dried before using for the first time.

After standing overnight, the samples are centrifugalized at 1800 r. p. m. for 30 minutes and the liquid is carefully poured off. It is advisable to wash the precipitate with 2 cc. of hydrogen sulfide water containing 1 per cent hydrochloric acid and recentrifugalize for 30 minutes. The liquid is poured off and to the copper sulfide which remains in the centrifuge tube 4 drops of fuming nitric acid are added. The tube is placed in a boiling water bath for 10 minutes. The sample is then cooled, diluted to about 5 cc., and 1 cc. of 20 per cent ammonium hydroxide added or enough to give a distinct odor. The solution is cooled, made up to exactly 10 cc., and mixed thoroughly.

It has been suggested that, if the precipitation of copper sulfide were carried out under pressure, both the rate of precipitation and the amount of precipitate formed should be increased. This does not seem necessary, however, since copper is quantitatively recovered by the above procedure when the precipitate is allowed to stand overnight. Furthermore, it would be impractical when the gas is introduced from a tank where it is under considerable pressure.

Microelectrolytic Method. The milk ash is dissolved in a minimum amount of 1 to 1 nitric acid, heating a little. The solution is transferred to a 15-cc. centrifuge tube with water and centrifugalized to remove the carbon, washed once with 2 cc. of water, recentrifugalized, and added to the first solution. The solution is brought to a definite volume (6 to 10 cc.) and mixed well. An aliquot is transferred to the electrolytic vessel. The amount should be just enough to cover the gauze cathode completely.

The electrolytic apparatus described by Pregl (*32*) was used, the apparatus with the exception of the electrodes being assembled from materials in the laboratory.

The cathode must be cleaned before each determination by treating with hot concentrated hydrochloric acid for 10 minutes. It is then rinsed with water, alcohol, and ether and dried over a small flame. The electrolytic vessel—a Pyrex tube of just the right diameter to receive the cathode—previously cleaned in cleaning solution, is filled with the proper amount of ash solution (about 5 cc.). The cathode is introduced and then a drop of alcohol added to prevent loss due to the vigorous bubbling. The anode is then placed in the tube and the connections are made with the circuit. The current is adjusted to 3 volts by means of a series resistance and the electrolysis run for 10 minutes, the voltage being kept between 2.7 and 3.1 during the entire electrolysis. The cell is heated by a microburner to nearly boiling, then the tube is allowed to cool during the remainder of the electrolysis. During the last 5 minutes the cell is cooled in a beaker of cold water.

After electrolysis is completed, the acid must be thoroughly washed from the cell without breaking the current (*31*). This is done by filling the cell with distilled water, introducing a pipet to which a capillary tube has been attached so that it will reach to the bottom of the cell without touching the cathode, and drawing off the liquid down to the level of the gauze cathode. By repeating this process a number of times, using about 70 cc. of

water, the acid is washed completely from the cell. This is indicated when bubbles cease to arise from the anode. The anode and then the cathode are carefully withdrawn and the latter is placed in a 50-cc. beaker and moistened with 1 cc. of 1 to 1 nitric acid. The beaker is heated and tilted so that by rotating the cathode the hot acid is brought into contact with the whole surface. The cathode is then transferred to a 15-cc. graduated centrifuge tube and thoroughly rinsed with about 5 cc. of distilled water. The cathode is removed and the copper solution from the beaker rinsed into the centrifuge tube. Two cubic centimeters of 20 per cent ammonium hydroxide are added (or enough to furnish an excess), and the volume is brought to 10 cc. and thoroughly mixed.

When analyzing products which may be highly contaminated with other metals, it is advisable to carry out a second electrolysis after the first deposit has been dissolved by reversing the current in 1 per cent nitric acid solution. This second deposit will be free from all other constituents of the milk ash. It appears essential for both precipitation methods that fresh ash solutions be used, since difficulties have sometimes been encountered with old solutions.

Colorimetric Estimation of Separated Copper. From this point the procedure is the same for both the sulfide and electrolytic methods. The ammoniacal solution, having been brought to 10 cc. and mixed well, is centrifugalized for 10 minutes to remove the slight turbidity which sometimes occurs upon adding the ammonia, and then transferred to another tube. This procedure removes the last traces of any interfering substances that might be present.

An aliquot containing from 0.001 to 0.005 mg. of copper is taken for the colorimetric estimation. The authors found that thin-walled, clear-glass, 15-cc. centrifuge tubes of even diameter are entirely satisfactory for the purpose. Two cubic centimeters of ammonia are added and the volume is brought to 10 cc.

One cubic centimeter of a 0.1 per cent aqueous solution of sodium diethyldithiocarbamate (Eastman) is added and the solution mixed well. The yellow color is compared immediately with the color in a set of standards prepared in the same manner from a copper sulfate solution containing 0.01 mg. of copper per cubic centimeter. This should be freshly prepared for each set of determinations from an accurately standardized stock solution containing 1 mg. of copper per cubic centimeter. A set of 9 standards covering the range from 0.001 to 0.005 mg. of copper with intervals of 0.0005 mg. is convenient. Smaller amounts than 0.0010 mg. of copper cannot be accurately determined, and in such cases it is necessary to ash a larger sample.

Critical Study of Methods

Experiments were carried out to determine the accuracy of the hydrogen sulfide method when applied to copper sulfate solutions or milk. The data in Tables III and IV show that copper is recovered quantitatively from both copper sulfate and milk ash solutions in amounts as small as 0.00196 to 0.00784 mg. by precipitation with hydrogen sulfide and removal of the precipitate by centrifugalization. In samples 4, 5, and 6 (Table IV) closely agreeing results were obtained when either 50 or 200 cc. of milk were evaporated. In the case of pasteurized milk, where the copper content is higher (sample 3), 25-cc. samples were sufficient. Table V gives the results obtained by three different investigators in this laboratory upon the same milk sample. Investigators 1 and 2, not having had occasion to use this method before, proceeded according to written instructions alone, whereas investigator 3 was thoroughly acquainted with the method. Good recovery of added copper was obtained in all three cases.

In Table VI are given results of comparative tests in which the same milks were analyzed by both the hydrogen sulfide and the electrolytic methods. In all cases except one (the milk from the Holstein cow) there is good agreement between the two methods. From a sample of certified milk 97 and 98 per cent of added copper were recovered by the sulfide and electrolytic methods, respectively.

In order to check the accuracy of the methods still further, copper deposited by electrolysis was weighed on the microbalance and subsequently dissolved and determined colorimetrically. This firmly established the accuracy of the colorimetric estimation of such minute amounts of copper.

Several difficulties were encountered in this work. In the first experiments the weight of the deposit on the cathode indicated from three to ten times as much copper as was found by colorimetric estimation. Contamination of the deposit by other constituents of the milk ash was ruled out, as the weight was the same after reversing the current and redepositing the copper—the method usually resorted to in eliminating

Table III. Copper Recovery from Copper Sulfate Solution

Sample	Copper Present	Copper Recovered	
	Mg.	*Mg.*	%
A	0.00196	0.002058	105
		0.001764	90
		0.002156	110
B	0.00392	0.003822	97
		0.004802	122
		0.003038	77
C	0.00588	0.004312	73
		0.005488	93
		0.005268	89
D	0.00784	0.00686	87
		0.007448	95
		0.007252	92

Table IV. Copper Recovered from Milk

Sample	Milk Ashed	Copper Added[a]	Copper Found	Added Copper Recovered
	Cc.	*Mg.*	*Mg.*	%
1	200	0.0	0.0123	..
	200	0.0	0.0113	..
	200	0.007	0.0181	96.3
	200	0.007	0.0196	104.2
2	50	0.0	0.0037	..
	50	0.0	0.0036	..
	50	0.0	0.0035	..
	50	0.0020	0.0049	87.7
	50	0.0039	0.0057	75.8
	50	0.0078	0.0100	87.4
3 (pasteurized)	25	0.0	0.0063	..
	25	0.0	0.0062	..
	25	0.0	0.0067	..
	25	0.0	0.0053	..
	25	0.0029	0.0099	107.2
4	50	....	0.073, 0.075, 0.071	..
	200	....	0.082, 0.066	..
5	50	....	0.042, 0.065	..
	200	....	0.055, 0.045	..
6	50	....	0.053, 0.067	..
	200	....	0.039, 0.045	..

[a] Copper added to milk sample in crucible before evaporating.

Table V. Comparison of Results of Three Investigators

Investigator	Control Milk		Control + 0.00296 Mg. of Copper per 50 Cc.		Added Copper Recovered[a]
	Mg./50 cc.	*P. p. m.*	*Mg./50 cc.*	*P. p. m.*	%
1	0.0023	0.046	0.0055	0.110	94.9
	0.0025	0.050	0.0049	0.098	
2	0.0022	0.043	0.0055	0.110	113.5
	0.0017	0.035	0.0051	0.101	
3	0.0027	0.054	0.0059	0.118	108.5
	0.0027	0.054	....	...	
Av.	0.0024	0.047	0.0054	0.107	...

[a] Average of two determinations.

Table VI. Comparative Tests with Hydrogen Sulfide and Electrolytic Method

Source	Hydrogen Sulfide Method	Microelectrolytic Method
	P. p. m.	*P. p. m.*
Uncontaminated milk from individual cows:		
Holstein	0.044, 0.038	0.072, 0.071
Guernsey	0.042, 0.046	0.046, 0.040
Jersey	0.052, 0.060	0.056, 0.072
Certified milk	0.136	0.124
0.2 p. p. m. of copper added (0.01 mg. to 50 cc.[a])	0.360, 0.300	0.310, 0.330
Pasteurized milk	0.32, 0.34, 0.335	0.25, 0.28, 0.30

[a] Per cent recovered: hydrogen sulfide method, 97.0; microelectrolytic method, 98.0.

Table VII. Comparative Tests to Show Accuracy of Methods

Sample	Electrolytic Method[a]		Hydrogen Sulfide–Electrolytic Method[b]: Cu deposited on cathode[d]		Hydrogen Sulfide–Electrolytic Method[b]: Cu deposit dissolved in HNO_3[e]		Hydrogen Sulfide Method[c]	
	Mg.	*P. p. m.*	*Mg.*	*P. p. m.*	*Mg.*	*P. p. m.*	*Mg.*	*P. p. m.*
Whole milk powder:								
Ashed in silica	0.0527	5.27	0.238	3.97	0.258	4.30	0.050	5.00
							0.0387	3.87
Ashed in platinum	0.0390	3.90	0.278	4.63	0.2724	4.54	0.0393	3.93
Certified milk:								
Ashed in silica	0.0139[f]	0.093	0.064	0.128	0.0484	0.097	0.0203[f]	0.135
							0.0128[g]	0.128
Ashed in platinum	0.0156[f]	0.104	0.064	0.128	0.0495	0.099	0.0229[g]	0.153
							0.0187[g]	0.187
Pasteurized milk:								
Ashed in silica	0.0649[g]	0.649	0.305	0.610	0.3125	0.625	0.0612[g]	0.612
Ashed in platinum	0.0638[g]	0.638	0.292	0.584	0.278	0.556	0.0616[g]	0.616
$CuSO_4$ solution (0.260 mg. Cu)	....	...	0.283	...	0.257	...	....	...
			109%		99%			
$CuSO_4$ solution (0.312 mg. Cu)	....	...						
			0.308[h]	...	0.312[h]	...	....	...
			99%		100%			

[a] 100 to 150 cc. of milk or 10 grams of milk powder ashed, dissolved in nitric acid, and electrolyzed. Carbamate colorimetric method used.
[b] 500 cc. of milk or 60 grams of milk powder ashed, CuS precipitated, dissolved in nitric acid, and electrolyzed.
[c] 100 to 150 cc. of milk or 10 grams of milk powder ashed, CuS precipitated and dissolved in nitric acid. Carbamate colorimetric method used.
[d] Copper deposited on cathode weighed on microbalance.
[e] Copper deposit (previously weighed) dissolved in nitric acid. Carbamate colorimetric method used.
[f] 150 cc. ashed.
[g] 100 cc. ashed.
[h] CuS not precipitated.

contamination. Sometimes the deposit on the cathode was black and treatment with nitric acid did not affect this color, indicating that platinum from the crucibles might be the source of contamination. An attempt therefore was made to precipitate the copper as the sulfide, dissolve it in nitric acid, and then electrolyze this solution. In this case the deposit showed only slightly more copper by weight than by colorimetric determination. Finally, a sample was ashed in a silica dish, the ash dissolved in nitric acid, and this solution electrolyzed. The weight of the copper deposit agreed with that found by ashing in platinum and separating the copper as sulfide before electrolyzing. These experiments indicate that platinum dissolved from the crucible by the milk ash was a source of contamination. However, this was not an interfering factor in the colorimetric estimation of the copper and became a problem only when it was desired to check the colorimetric method by direct microelectrolytic determination.

If the deposit was calculated as copper oxide, the results agreed closely with the colorimetric method and therefore the length of time and amount of heat necessary to dry the electrode were probably sufficient to oxidize the copper. Drying the electrode first with alcohol and ether reduced the time of heating over a flame from 15 minutes to 1 minute. No difficulty was experienced with losing copper by the alcohol and ether drying, in spite of the fact that Pregl (*32*), quoting Benedetti-Pichler, states that the reduced surface tension may cause the loss of some copper.

The error of the microbalance was 0.002 to 0.005 mg.; therefore, for gravimetric determination, the amount of copper present should be more than 0.05 mg. to insure at least 90 per cent accuracy. Using the 500 cc. of milk or 60 grams of milk powder necessary for this amount of copper, it was impossible to keep the volume of the ash solution small enough for the microelectrolytic cell. Therefore the copper was first separated with hydrogen sulfide and the dissolved sulfide electrolyzed. To rule out the possibility of other metals besides copper being deposited by the electrolysis, the deposit was dissolved after electrolysis by reversing the current (using 1 per cent nitric acid as the electrolyte) and was redeposited on a second cathode which had been previously weighed. The electrode was reweighed after drying carefully, the increase in weight giving the amount of copper in the sample. This copper was then dissolved from the electrode and also determined colorimetrically.

Three samples were chosen for the comparative experiments —one of pasteurized milk, one of certified milk, and one of milk powder—and analyzed by three different methods: the hydrogen sulfide method, the microelectrolytic method, and the method just described, a combination of the sulfide and electrolytic methods in which the copper was determined both gravimetrically and colorimetrically. Table VII gives results of duplicate determinations that were carried out upon each sample, one of the duplicates being ashed in platinum and the other in silica, and copper sulfate solutions which serve as a control on the gravimetric method. The copper contents as determined by all three methods are generally in very good agreement. In the samples of certified milk analyzed by the sulfide method three out of the four determinations are somewhat higher than by the other two methods. Where the copper content is as low as this, greater accuracy may be insured by using larger samples (200 cc.).

The sulfide method seems to have several points in its favor for the routine determination of copper in dairy products: It is more accurate for samples with a very low copper content, as very small amounts of copper are not quantitatively deposited by this particular method of electrolysis; it is more generally available to laboratories making routine copper analyses; it requires less constant attention from the analyst; and when a large number of determinations are being made at one time it is less time-consuming.

Application of Sulfide-Carbamate Method

In Table VIII are given the copper contents of a series of raw milks, pasteurized milks, milk powders, and one sample of buttermilk. The copper contents of eighteen samples of raw milk collected directly in glass, thus eliminating any possibility of contamination, were found to vary between 0.051 and 0.132 p. p. m. with an average of 0.077 p. p. m. The samples collected from different states show no significant variations except those from New York. These samples were all from the Cornell University Dairy Farm and seem to be slightly higher in copper content. However, such a small variation is probably not significant. Analyses of seven samples of pasteurized milk from different dairies had copper contents of 0.088 to 0.741 p. p. m. Greater variation between samples is to be expected in pasteurized milk than in raw milk, and is apparent in these results. This is due to the use of different kinds of metallic equipment in the dairy and the degree of corrosion it may have undergone. The sample showing only 0.088 p. p. m. of copper, which is in the range of uncontaminated raw milk, came from a dairy which had been in operation only a few months and where the equipment was probably in exceptionally good condition.

Table VIII. Copper Content of Raw, Pasteurized, and Dried Milks

Description of Sample	Source	Amount Ashed	Copper Det. 1	Copper Det. 2	Average
		Cc.	*P. p. m.*	*P. p. m.*	
Raw[a]	Connecticut	200	0.066	0.067	0.067
		200	0.061	0.078	0.070
		200	0.074	0.071	0.073
Raw	New York	200	0.110	0.098	0.104
		200	0.089	0.092	0.091
		200	0.116	0.113	0.115
		200	0.123	0.141	0.132
Raw	Kentucky	200	0.074	0.082	0.078
		200	0.059	0.060	0.060
		200	0.064	0.074	0.069
		200	0.074	0.061	0.068
		200	0.098	0.104	0.101
		200	0.059	0.062	0.061
Raw	Maryland	200	0.069	...	0.069
		200	0.072	...	0.072
		200	0.051	...	0.051
		200	0.064	...	0.064
		200	0.051	...	0.051
Av.					0.077
Pasteurized	Connecticut	200	0.190	0.202	0.196
Pasteurized	Maryland[b]	50	0.090	0.086	0.088
		50	0.108	0.123	0.116
		50	0.260	0.254	0.257
		50	0.750	0.731	0.741
Pasteurized	District of Columbia[c]	50	0.170	0.162	0.166
		50	0.223	0.196	0.210
Av.					0.253
		Grams			
Dried	1	10	1.37	...	...
Dried (partially defatted)	2	10	1.54	...	...
Dried	3	10	17.15	...	...
Dried	4	10	9.07	...	...
Dried skim	5	10	3.63	...	...
Buttermilk	Maryland	25	0.549	...	...

[a] All samples of raw milk were from individual cows and were milked directly into glass.
[b] From four different dairies.
[c] From two different dairies.

Five samples of dried milk showed copper contents varying from 1.37 to 17.15 p. p. m. The data in Table IX show that large quantities of copper may enter milk during treatment in copper equipment. The use of well-tinned equipment diminishes this take-up considerably.

Table IX. Copper Contents of Samples Taken during Manufacture of Milk Powder

Description of Sample	Solids Content	Copper Content
	%	*P. p. m.*
PLANT I, SERIES 1. HANDLED IN REGULAR COPPER EQUIPMENT		
Preheated at 142° F.	8.64	0.719
Held in hot well 30 min. at 175° F.	8.60	2.144
Condensed 1 hr. at 132° F. Held in pan 18 min. after cooling	23.87	12.25
After cooling over surface cooler	24.02	11.23
Finished product, spray process	96.70	30.46
PLANT I, SERIES 2. HANDLED IN NEWLY TINNED EQUIPMENT		
Preheated at 142° F.	8.67	0.604
Held in hot well 30 min. at 175° F.	8.66	0.493
Condensed for 1 hr. at 132° F.	25.00	2.166
After cooling over surface cooler at 52° F.	24.98	2.70
Finished product, spray process	96.65	12.74
Skimmilk control, both series	8.66	0.096
PLANT II		
Skimmilk entering copper hot well	8.71	0.28
Last of skimmilk leaving hot well	8.70	0.95
During condensing in copper vacuum pan	24.87	7.10
Condensed	26.49	5.63
Condensed and cooled	26.21	6.37
Powder (roller) (approx.)	98.00	26.66
Skimmilk control	8.75	0.32

The copper contents of uncontaminated milk samples as determined in this laboratory are lower than those reported by most of the investigators in Table I, but the average agrees well with the work of McFarlane (*27*) who also eliminated the use of filter papers. The results of Grendel (*19*), who used a microelectrolytic method of separating the copper (making necessary two filtrations) along with the carbamate method of colorimetric estimation, were slightly higher than the authors' and slightly lower than those of Elvehjem, Hart, and Steenbock (*14*), who used three filter papers in their procedure. The authors believe that the use of filter paper causes a certain amount of contamination, but this would not account for the total difference. McFarlane obtained higher results on the same milk by the Biazzo method as used by Elvehjem, Hart, and Steenbock, than he did with the carbamate method.

As has been pointed out (*14*), the results of Supplee and Bellis (*41*) were too high, owing to contamination from porcelain crucibles. The results of other workers (*25*, *33*) who used the same technic are subject to the same criticism. Keil and Nelson (*24*) found 0.24 p. p. m. of copper in one sample of milk collected in glass, but the details of the method were not given. The work of Guthrie, Roadhouse, and Richardson (*20*) and Davies (*11*) was done upon raw milk which had been in contact with tinned containers and so was subject to metallic contamination. The method of Zondek and Bondmann (*52*), discussed above, has not been used for the analysis of milk by other investigators.

Thus the summary of the results given in Table I shows that with the development of more accurate methods of analysis the copper content of uncontaminated milk is actually much less than the early results of Supplee and Bellis indicated. In the method of McFarlane and that developed in this laboratory, where contamination from outside sources has been reduced to a minimum, the copper content of milk has been found to vary between 0.068–0.096 and 0.051–0.132 p. p. m., respectively.

In the analysis of pasteurized or dried milk where the copper content is higher because of contact with metals during handling and processing, naturally the variation between different methods will not be so apparent as in the analysis of uncontaminated raw milk. It is not well to attempt to compare results of different investigators, because the amount of variation due to exposure to different types of metallic equipment is great. The authors' results show that in some cases the copper content of pasteurized milk may be but slightly higher than that of raw milk.

Conclusions

The sulfide-carbamate method devised by the authors for the estimation of copper in milk is accurate for amounts as small as 0.002 mg. of copper, making it possible to use from 25- to 200-cc. samples for analysis. The accuracy and simplicity of this method make it superior to the methods generally in use for the determination of copper in milk.

The copper content of uncontaminated raw milk was found to range from 0.051 to 0.132 p. p. m., with an average of 0.077 p. p. m. for eighteen samples. The copper content of seven samples of pasteurized milk varied from 0.088 to 0.741 p. p. m. The copper content of five samples of dried milk varied from 1.37 to 17.15 p. p. m.

Milk exposed to copper equipment takes up considerable copper during the process of manufacture of milk powder.

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Determination of Fluorine in Drinking Water

Comparison of Several Methods and Establishment of Toxic Concentration by These Methods

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SINCE the discovery that fluorine in drinking water (*8*) is the cause of mottled enamel of teeth, much interest has been manifested in the analysis of water for this element. When the first studies of the cause of mottled enamel were made at the University of Arizona in 1930, the volatilization method of Jacob, Ross, and Reynolds (*6*) for the determination of fluorine in rock phosphate was adapted to water analysis, and used in determination of the fluorine present in waters known to cause mottled enamel. This method consisted essentially of the distillation of fluorine as silicon tetrafluoride from the dry water residue into water, and titration of the hydrofluosilicic acid thus formed with a standard base. From the use of this method, it appeared that the minimum concentration of fluorine in water which would produce mottled enamel lay between 0.72 and 2.0 parts per million.

This preliminary work was followed by a more intensive study of the occurrence of mottled enamel and its correlation with the concentration of fluorine in water supplies (*9*). In 1931 practically all parts of Arizona were visited, the teeth of the native inhabitants examined, and the water supply was sampled for analysis. Subsequently the fluorine analyses were made by the Fairchild method (*3*) as modified and used by Churchill (*1*). In this method the fluorine combines with ferric iron which is added in excess as ferric chloride. The uncombined iron is determined iodometrically and the amount of fluorine is calculated.

The analysis of about 160 samples of water by this method showed a fluorine content ranging from 0.2 to 12.6 parts per million. Endemic areas in which mottled enamel was of the rather severe type were found to be using water with a fluoride content in excess of 5.0 parts per million. The minimum concentration of fluorine in water which was observed to produce mottled enamel appeared to lie between 2.0 and 2.7 parts per million. With this information at hand it was possible to predict with considerable accuracy the probable effect of any water on the teeth.

As a result of the great interest in the problem of fluorosis, other methods of fluorine determination have since been developed and the limitations of the Fairchild method, when applied to water, brought out. Foster (*5*) has pointed out that the Fairchild method of analysis gives high results when no correction is made for sulfates, for they have an effect similar to fluorides. The writer has also noted that organic matter in waters renders the Fairchild method unreliable because it has an iodine-consuming power which leads to a high fluorine result.

It is the purpose of this paper therefore to compare the results obtained by some of the more recently developed methods of fluorine analysis, and to establish the toxic

Table I. Fluorine Content of Potable Waters Correlated with Their Effect upon Teeth[a]

Location	Method of Analysis: Fairchild	Foster	Willard	Sanchis	Location	Method of Analysis: Fairchild	Foster	Willard	Sanchis
A. Waters which cause mottled enamel									
Ajo	5.8	2.2	2.4	2.8	N. Gila School	9.1	1.9	2.4	2.4
Aztec	12.0	7.2	6.8	8.0	Oracle	3.0	1.1	1.5	1.3
Buckeye	2.4	1.5	1.2	1.3	Hayden (rural)	7.5	3.0	3.2	...
Cochise	2.0	0.9	0.9	...	Safford (rural)	3.0	1.1	...	1.3
Concha	7.5	3.9	4.7	...	Roll	8.7	4.7	...	5.0
Douglas	5.2	2.4	2.4	2.5	Roll School	3.3	1.3	1.3	1.5
Eager	1.8	0.9	0.9	...	Roosevelt School Dist.	3.5	1.5	1.9	1.7
Florence	2.8	0.9	0.9	1.1	San Xavier	3.0	0.9	1.0	0.9
Gila Bend	10.6	6.8	6.7	6.8	Sentinel	9.3	6.0	5.5	5.8
Gila River	3.0	0.9	1.0	...	St. David	4.6	1.1	1.8	1.6
Joseph City	2.8	1.0	1.0	0.9	St. David	6.0	3.6	3.4	3.4
Hayden	3.0	1.3	...	1.4	Topock	4.7	1.0	...	2.8
Laveen	2.5	1.6	1.3	1.5	Wilson, Ida.	16.8	13.2	11.1	...
Mammoth	6.0	3.7	3.9	4.0	Winkleman	2.8	1.1	1.1	1.0
Mesa (rural)	3.1	1.0	1.1	1.0	Sentinel	7.7	5.9	4.5	4.8
Menlo Park	2.7	1.0	1.1	1.0					
B. Waters which do not cause mottled enamel									
Avondale	1.8	...	0.4	...	Pomerene	1.4	0.5	0.3	0.5
Benson	0.9	0.4	0.3	0.3	Pomerene School	0.9	0.5	0.6	0.8
Chandler	2.1	0.7	0.8	0.8	Prescott	1.1	0.2	0.6	0.1
Clarkdale	1.2	0.3	0.5	0.2	Red Rock	1.0	0.6	0.5	0.7
Concha (spring)	0.9	0.4	0.3	0.3	Safford	0.5	0.4	0.2	0.4
Fairbanks	0.3	0.1	0.4	0.3	Sonoita	0.6	...	...	0.3
Flagstaff	1.1	0.5	0.3	0.2	Superior	1.1	0.3	0.4	0.3
Holbrook	2.5	0.4	0.5	0.3	Tombstone	0.2	0.1	0.3	0.0
Jerome	1.1	0.2	0.3	0.1	Wickenberg	1.5	0.1	0.4	0.2
Miami	1.0	0.1	...	0.3	Willcox	1.2	0.3	0.4	0.2
Morenci	1.7	0.4	0.6	0.4	Winslow	0.7	0.2	0.2	...
Nogales	1.9	0.6	...	0.7	Yuma	2.0	0.4	0.4	...
Pima	0.8	0.5	0.2	0.5					

[a] All fluorine solutions used as standards were made from sodium fluorite obtained from the U. S. Bureau of Standards.

concentration of fluorine in water when the analysis is made by any of these methods.

Experimental

The methods investigated include those of Willard and Winter (*11*), Foster (*5*), and Sanchis (*7*), and the results of analysis by these methods are compared with each other and with the Fairchild method.

In the method of Willard and Winter (*11*) the fluorine is distilled off as hydrofluosilicic acid in the presence of glass beads and perchloric acid and the distillate is titrated with thorium nitrate, using zirconium nitrate and alizarin red or alizarin red alone as an indicator.

The Foster method (*4*) assumes that iron combines with fluorine to form the complex Na_3FeF_6, which does not react perceptibly with ammonium thiocyanate to give the characteristic red color of ferric thiocyanate. Ferric chloride is therefore added to the sample and the excess determined colorimetrically. In this method, ions such as sulfates and chlorides which have the ability to remove iron from reaction are compensated for by adding additional iron to the solution.

Sanchis (*7*) also used alizarin red and zirconium nitrate as an indicator in his method of fluorine analysis. The method is a modification of the Thompson and Taylor (*10*) method for the determination of fluorine in sea water. In the adaptation for the analysis of fresh water, chloride and sulfate effects up to 500 parts per million are nullified by the addition of hydrochloric and sulfuric acids.

In order to determine the minimum concentration of fluorine in water which would definitely mottle the teeth of those who drink the water during the period of formation of their permanent teeth, the fluorine content of waters of known association with this dental defect were tested by the methods described above. The results of these analyses correlated with their effect upon teeth are presented in Table I.

Further evidence is given that the results of fluorine analyses of water by the Fairchild method are abnormally high. However, the fluorine content of a given water as analyzed by the methods of Willard, Foster, or Sanchis is essentially of the same order. For example, the fluorine content of water from the rural Mesa district was found to be 1.1 parts per million by the method of Sanchis, 1.0 by the Foster method, and 1.1 by the method of Willard. The analysis of this same water by the Fairchild method gave a result about three times higher (3.1 p. p. m.)

The results of the analysis of 55 waters by these four methods are grouped into two classes: waters which are known to be associated with mottled enamel, and those which have been found not to cause mottled enamel. This division is based on tooth examinations made by Smith (*9*).

The 29 waters associated with mottled enamel, as analyzed by the Foster, Willard, and Sanchis methods, have a fluorine content varying from 0.9 to 13.2 parts per million. Twenty-five waters which did not cause mottled enamel had fluorine contents ranging from 0.1 to 0.8 part per million.

Severe mottled enamel of the deeply stained and pitted type appears to be associated with waters containing well over 2.0 parts per million of fluorine. Waters containing from 1 to 2 parts per million were always associated with a mild to moderate type of this dental defect. The lower limit of toxic fluorine concentration—i. e., concentration in water which will produce a very mild type of mottled enamel—appears to be from 0.9 to 1 part per million. It was noted also that other waters with a fluorine content of 0.7 to 0.8 part per million did not have a toxic effect upon the teeth—for example, the water supply of the city of Chandler. This community, however, is surrounded by areas in which mottled enamel does occur and in all probability has a fluorine content which is just below the toxic concentration.

It is difficult to establish the exact fluorine concentration in a water supply which will damage the teeth of its users, for other factors such as quantity of water consumed, length of time the water was used, and perhaps nutritional conditions of the subjects are variable. However, the evidence at hand indicates strongly that any water with a fluorine content of 0.9 part per million or over (when analyzed by the Foster, Willard, or Sanchis methods) is dangerous from the standpoint of probable damage to the teeth. No Arizona water has yet been found containing as much as 1.0 part per million of fluorine which has not been demonstrated to cause mottled enamel, and no water with a fluorine content less than 0.8 part per million has been found to be associated with mottled enamel.

As Dahle (*2*), associate referee for the Association of Official Agricultural Chemists, found little difference in results obtained between the Steiger and Foster methods, it is perhaps safe to conclude that the toxic concentration of fluorine is similar when determined by the Foster, Willard, Sanchis, or Steiger methods, and has as its lower limit 1.0 part per million or slightly less.

Summary and Conclusions

A comparison of the fluoride content of 44 waters has been made, using the Fairchild, Foster, Willard, and Sanchis methods.

Results obtained by the Foster, Willard, and Sanchis methods are in close agreement.

The Fairchild method gives results which average two to three times higher than results by other methods.

Concentrations of fluorine of 0.9 to 1.0 part per million and greater (Foster, Willard, or Sanchis methods) have been found associated with mottled enamel.

Concentrations of fluorine as high as 0.7 to 0.8 part per million (Foster, Willard, or Sanchis methods) have been found in waters not associated with mottled enamel.

No water has been found containing more than 1.0 part per million (Foster, Sanchis, or Willard methods) which is not definitely associated with mottled enamel.

No water has been found containing less than 0.8 part per million which is known to cause mottled enamel.

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Nomogram for Centrifugal Force

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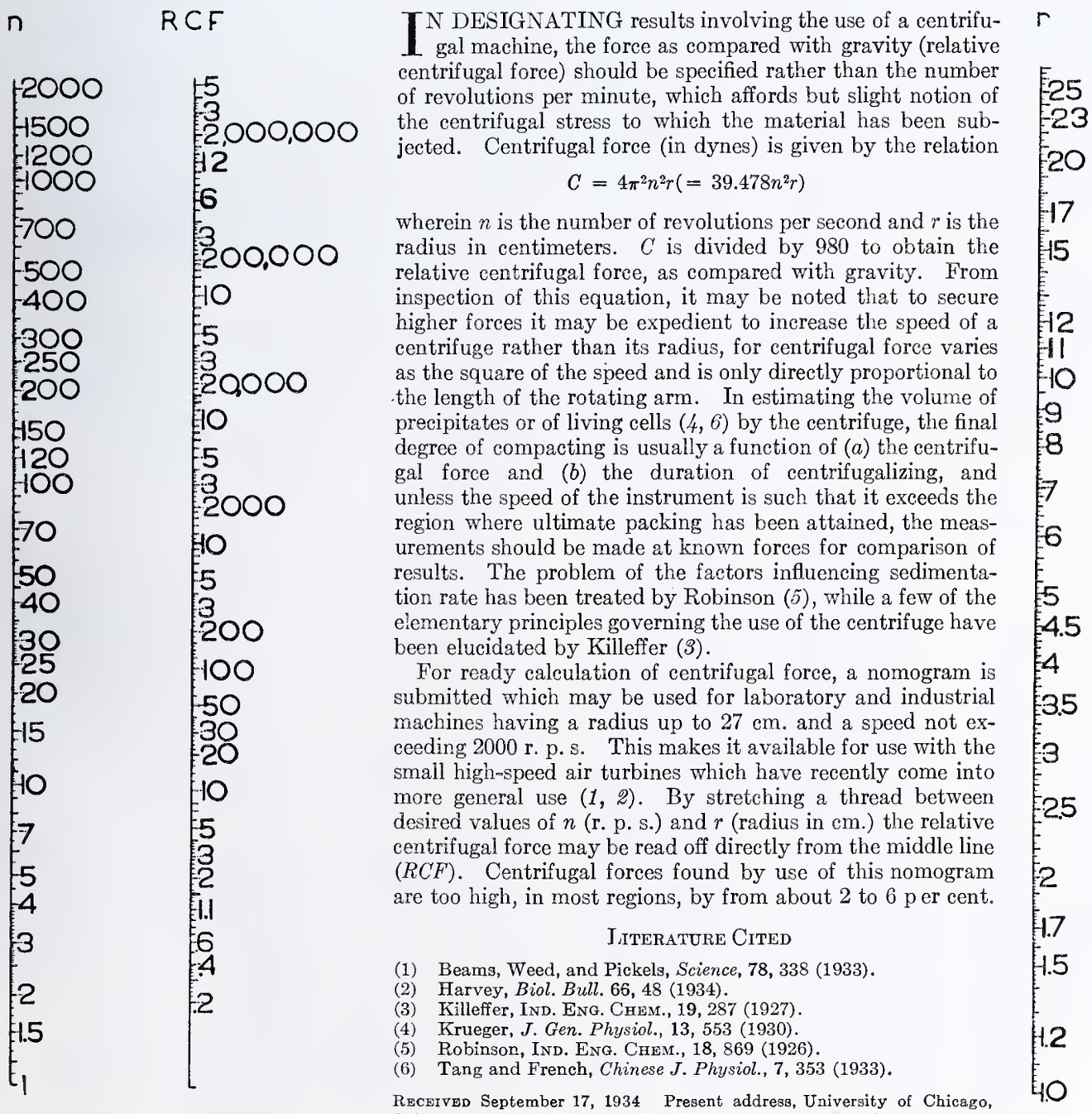

In designating results involving the use of a centrifugal machine, the force as compared with gravity (relative centrifugal force) should be specified rather than the number of revolutions per minute, which affords but slight notion of the centrifugal stress to which the material has been subjected. Centrifugal force (in dynes) is given by the relation

$$C = 4\pi^2 n^2 r (= 39.478 n^2 r)$$

wherein n is the number of revolutions per second and r is the radius in centimeters. C is divided by 980 to obtain the relative centrifugal force, as compared with gravity. From inspection of this equation, it may be noted that to secure higher forces it may be expedient to increase the speed of a centrifuge rather than its radius, for centrifugal force varies as the square of the speed and is only directly proportional to the length of the rotating arm. In estimating the volume of precipitates or of living cells (*4*, *6*) by the centrifuge, the final degree of compacting is usually a function of (*a*) the centrifugal force and (*b*) the duration of centrifugalizing, and unless the speed of the instrument is such that it exceeds the region where ultimate packing has been attained, the measurements should be made at known forces for comparison of results. The problem of the factors influencing sedimentation rate has been treated by Robinson (*5*), while a few of the elementary principles governing the use of the centrifuge have been elucidated by Killeffer (*3*).

For ready calculation of centrifugal force, a nomogram is submitted which may be used for laboratory and industrial machines having a radius up to 27 cm. and a speed not exceeding 2000 r. p. s. This makes it available for use with the small high-speed air turbines which have recently come into more general use (*1*, *2*). By stretching a thread between desired values of n (r. p. s.) and r (radius in cm.) the relative centrifugal force may be read off directly from the middle line (*RCF*). Centrifugal forces found by use of this nomogram are too high, in most regions, by from about 2 to 6 per cent.

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A Critical Study of Cacotheline for the Detection of Tin

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THE use of organic reagents for the detection of metal ions is becoming more and more prevalent, and the published literature dealing with these often implies, if not asserts, that a test is specific when the reactions have been only partially investigated. Leuchs (*4*), during a study of some of the derivatives of brucine, found that the stannous ion produced a characteristic amethyst color with cacotheline. This color reaction was subsequently proposed by Gutzeit (*2*) and Feigl (*1*) as a test for the stannous ion, Feigl classifying it as a specific test of sufficient sensitivity to warrant its serious consideration as a valuable means for the detection of tin. However, the published work on cacotheline does not completely describe the limitations as to sensitivity and specificity, or the difficulty likely to be encountered from interfering substances. This investigation was undertaken in order to test out thoroughly the sensitivity and specificity of the cacotheline reagent for tin in the presence of ions commonly encountered in analytical procedure.

Apparatus. A simple colorimetric apparatus was developed for testing the reagent and proved satisfactory for making rapid and accurate determinations. This consists of a constant source of illumination, with a diffusing type of reflecting surface for transmitting the light through a bank of test tubes (15 × 125 mm.).

Cacotheline Reagent. Cacotheline[1] was prepared from brucine by the action of nitric acid (*5*). A solution of cacotheline was made by dissolving 0.25 gram in 100 cc. of water. (It is desirable to preserve the reagent in a dark bottle.)

Procedure. Solutions of various ions in 10-cc. volumes were treated with 0.1 cc. of the cacotheline reagent, allowed to stand until maximum color developed, and then compared in the colorimeter in order to ascertain any difficulty from interfering substances.

[1] Small quantities (1 to 10 grams) of cacotheline may be obtained from Lewis S. Maxfield, 37 Dorothy St., Hartford, Conn.

Experimental

Preliminary trials showed the test to have a sensitivity to stannous tin in water solution of 1.6×10^{-5} *M*, or approximately 2 parts per million. In hydrochloric acid solution (30 milliequivalents) the sensitivity increased to 0.8×10^{-5} *M* or 1 part per million. In nitric acid (30 milliequivalents) the test was inhibited, while in sulfuric acid (30 milliequivalents) the test was relatively insensitive, 60 parts per million of stannous ion being required to produce detectable color.

It was observed that the rate of color development was different in water and hydrochloric acid media. The colors developed at low concentrations of stannous ion in water solution required 0.75 hour to reach a maximum, whereas in 30 milliequivalents of hydrochloric acid the maximum color developed in 15 minutes. The colors developed were not permanent, but disappeared after several hours.

The results of tests for stannous tin (concentration 1.6×10^{-5} *M* in water and 0.8×10^{-5} *M* in hydrochloric acid) in the presence of various other ions are given in Table I. No concentrations higher than 0.01 *M* were employed, and tests were made in hydrochloric acid solution as well as in water, since the presence of free hydrochloric acid enhanced the sensitivity of the test.

Of the cations tested, the antimonous ion alone gave a color with the cacotheline reagent, and this only in concentrations equal to or greater than 0.01 *M*. Reducing ions, such as bisulfite, hydrosulfite, and sulfite, gave a color reaction, which the authors found depended largely on the concentrations

Table I. Tests for Stannous Tin in Presence of Other Ions

Ion	Concentration *M*	Results: Water solution	Results: Hydrochloric acid solution (30 ml. eq.)
Aluminum	0.01	No interference	No interference
Ammonium	0.01	No interference	No interference
Antimonic	0.01	No interference	No interference
Antimonous	0.01	Very slight interference	Very slight interference
Barium	0.01	No interference	No interference
Beryllium	0.01	No interference	No interference
Bismuthous	0.01	No interference	No interference
Cadmium	0.01	No interference	No interference
Calcium	0.01	No interference	No interference
Cerous	0.01	No interference	No interference
Cesium	0.01	No interference	No interference
Chromic	0.0003	Interferes, inhibits test	Interferes, inhibits test
Chromous	0.001	Interferes, inhibits test	Interferes, inhibits test
Cobaltous	0.00025	Interferes, cobaltous ion color	Interferes, cobaltous ion color
Cupric	0.0001	Interferes, inhibits test	Interferes, inhibits test
Cuprous	0.0001	Interferes, inhibits test	Interferes, inhibits test
Ferric	0.0025	Interferes, ferric ion color	Interferes, ferric ion color
Ferrous	0.01	No interference	No interference
Lanthanum	0.01	No interference	No interference
Lead	0.01	No interference	Slight interference, cloudiness of $PbCl_2$
Lithium	0.01	No interference	No interference
Magnesium	0.01	No interference	No interference
Mercuric	0.001	Interferes, inhibits test	Interferes, inhibits test
Mercurous	1.6×10^{-5}	Interferes, inhibits test	Interferes, inhibits test
Nickelous	0.005	Interferes, nickelous ion color	Interferes, nickelous ion color
Potassium	0.01	No interference	No interference
Rubidium	0.01	No interference	No interference
Silver	1.6×10^{-5}	Interferes, inhibits test	Interferes, inhibits test
Sodium	0.01	No interference	No interference
Strontium	0.01	No interference	No interference
Thallous	0.01	No interference	Slight interference, cloudiness of TlCl
Thorium	0.01	No interference	No interference
Titanous	0.001	Interferes, inhibits test	Interferes, inhibits test
Uranyl	0.01	No interference	No interference
Zinc	0.01	No interference	No interference
Acetate	0.01	No interference	No interference
Arsenate	0.01	No interference	No interference
Arsenite	0.01	No interference	No interference
Bisulfite	0.0005	Interferes, reacts with cacotheline	No interference
Chloride	0.01	No interference	No interference
Chromate	1.6×10^{-5}	Interferes, inhibits test	Interferes, inhibits test
Hypophosphite	0.01	No interference	No interference
Hydrosulfite	0.001	Interferes, reacts with cacotheline	Interferes, gives amethyst color
Molybdate	0.005	Interferes, color of lower oxides of molybdenum	Interferes, color of lower oxides of molybdenum
Nitrate	0.01	No interference	No interference
Nitrite	1.6×10^{-5}	Interferes, inhibits test	Interferes, inhibits test
Phosphate	0.01	No interference	No interference
Selenite	0.001	Interferes, inhibits test	Interferes, inhibits test
Sulfate	0.01	No interference	No interference
Sulfite	0.001	Interferes, inhibits test	Interferes, color develops but fades rapidly
Vanadate	0.0025	Interferes, vanadate ion color	Interferes, vanadate ion color

involved. The action of these ions on cacotheline has been noted by Leuchs and co-workers (*3*, *6*).

A water solution of the bisulfite ion at concentrations above 0.0001 *M* decolorized 0.1 cc. of the cacotheline reagent, while in hydrochloric acid solution even at the maximum concentration (0.01 *M*) no change of color was noticed until after 15 minutes, when a detectable amethyst color was observed.

The hydrosulfite ion in water solution at concentrations below 0.0001 *M* caused no change in the cacotheline color, but from 0.0001 *M* to 0.001 *M* the cacotheline color was destroyed. From 0.001 *M* to 0.005 *M* a fugitive amethyst color of 15 minutes' duration developed, while from 0.005 *M* to 0.01 *M* destruction of the cacotheline color again occurred. In hydrochloric acid solution at concentrations up to 0.0001 *M* there was no change in the cacotheline color. Above this concentration a fugitive amythyst color of approximately 15 minutes' duration was produced and at concentrations approaching 0.01 *M* amorphous sulfur was precipitated.

The sulfite ion in water solution produced no change in the cacotheline color. In hydrochloric acid solution a concentration of 0.01 *M* caused a detectable amethyst color after 15 minutes. Lower concentrations produced no change in color.

Among the substances that interfere with the cacotheline test are oxidants, such as the mercuric, chromate, and chromic ions, and nitric acid. Reductants, such as the titanous, sulfite, hydrosulfite, and bisulfite ions, interfere when present in small concentrations. Colored ions, such as the cobaltous, cupric, cuprous, ferric, nickelous, and vanadate ions, interfere when present in sufficient concentrations. Certain other ions, such as molybdate, react with the stannous tin and prevent the test.

Where the maximum concentration used (0.01 *M*) gave no interference, there was no indication that there would be interference in higher concentrations, except in the case of the antimonous and hypophosphite ions.

Conclusions

The cacotheline test for tin cannot be regarded as specific, although it should prove useful for the detection or confirmation of the presence or absence of small amounts of tin where the conflicting substances are either absent or have been reduced in concentration to below those noted in Table I. The presence of hydrochloric acid was found to increase the sensitivity of the test. The maximum sensitivity of the cacotheline test for tin was found to be from 1 to 2 parts per million.

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Spectrophotometric Determination of Manganese in Steel

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A NUMBER of methods have been worked out for the colorimetric determination of manganese, based upon the oxidation of the manganese to permanganate and comparison of the color of the resulting solution with the colors of a series of standard permanganate solutions. The oxidation has been accomplished in various ways, the most important of which are by the use of sodium bismuthate (*2*), ammonium persulfate in the presence of silver nitrate (*11*, *17*), lead dioxide (*14*), and potassium periodate (*18*). Permanganate color standards, with the exception of those made by the periodate oxidation, are not stable enough to permit making permanent standards which may be used day after day in routine analyses. Hence the writer proposed to avoid their use entirely by the development of a spectrophotometric method for manganese.

The spectrophotometric method depends upon the fact that the percentage transmittancy of light at a given wave length for a permanganate solution is a function of the manganese concentration. If a reference curve is constructed by plotting the percentage transmittancy at the given wave length of a series of standard permanganate solutions against the known manganese concentrations, it should be possible to convert the percentage transmittancy of an unknown permanganate solution into manganese concentration by use of the curve. Main and Locke (*10*) have determined protein nitrogen similarly by measuring the light absorption at a given wave length of the nesslerized solution and converting this value into milligrams of nitrogen per 100 ml. by use of their reference curve relating absorption with concentration. Davis and Sheard (*3*) have determined hemoglobin in blood spectrophotometrically, and recently Sanford, Sheard, and Osterberg (*16*) have described an instrument called the photelometer, by use of which the intensity of the light transmitted by a colored solution is correlated with the concentration of the constituent responsible for the color. With it they have determined hemoglobin, blood sugar, and creatinine. Using a Pulfrich spectrophotometer in a somewhat similar manner, Pucher, Vickery, and Wakeman (*15*) have determined malic acid in plant tissues.

Separation and Determination of Manganese

In applying the spectrophotometric method to the determination of manganese in steel it was necessary to find a satisfactory procedure for separating the manganese from iron and other color-producing metals, since the color caused by the presence of these metals in the solutions would modify the transmittancy of the permanganate solution. Addition of phosphoric acid to decolorize the iron was not advisable, since this acid interfered with the bismuthate oxidation (*7*) and did not decolorize any chromium, nickel, or cobalt that might be present.

Precipitation of the manganese as hydrated manganese dioxide by boiling with potassium or sodium chlorate in concentrated nitric acid solution (*1*, *4*) proved to be very unsatisfactory, as much of the manganese was left in solution. A modification of this method as proposed by James (*5*) was likewise unsatisfactory, for in addition to incomplete precipitation of the manganese there was an unaccountable oxidation to permanganate.

After slight modification, von Knorre's method (*6*, *8*) gave

excellent results. It makes use of the fact that hydrated manganese dioxide is precipitated when manganous sulfate is boiled with a large excess of ammonium persulfate in 1 to 50 sulfuric acid solution. Zinc, chromium, nickel, cobalt, and moderate amounts of tungsten, molybdenum, or phosphorus

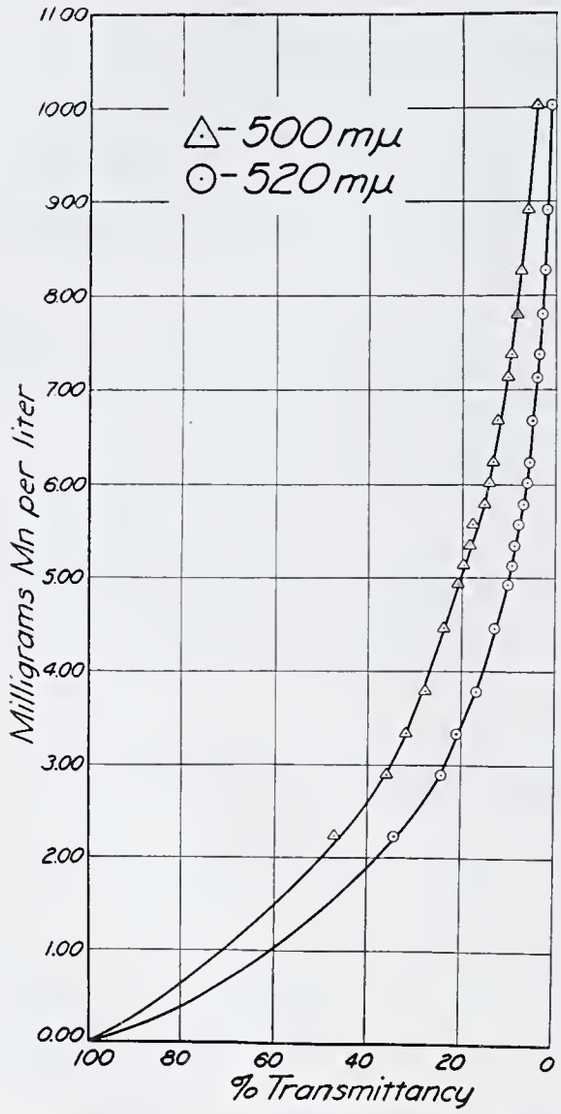

FIGURE 1. REFERENCE CURVES RELATING CONCENTRATION OF MANGANESE AND TRANSMITTANCY OF LIGHT AT 500 AND 520 Mμ OF PERMANGANATE SOLUTION IN A 5-CM. TUBE

The curves for 540 and 560 mμ are similar to those for 500 and 520 mμ.

do not interfere (*8*). The modification consists in the use of two additional 5-gram portions of persulfate, followed by boiling periods of 5 and 10 minutes, respectively. Von Knorre used a total of only 15 grams of persulfate, but this amount failed to give complete precipitation in the present work.

The manganese dioxide precipitate after filtration on a Gooch crucible was dissolved by reduction with sodium bisulfite in nitric acid solution. The manganese was then oxidized to permanganate with sodium bismuthate in the cold, and, after filtration on a Gooch crucible to remove the asbestos and excess bismuthate, the permanganate filtrate was made up to 1000 ml. at 25° C. To test the completeness of the separation of the manganese from the iron, the manganese was determined titrimetrically, using an aliquot of the solution, by adding excess standard solution of Mohr's salt and titrating the excess with 0.05 *N* solution of potassium permanganate. The results obtained on Bureau of Standards steel samples are given in Table I.

The transmittancies of light at wave lengths of 500, 520, 540, and 560 mμ were determined on another portion of the permanganate solution in a 5-cm. tube using the Keuffel and Esser color analyzer described by Mellon and Martin (*13*) and used by the writer in previous work (*12*). All data were obtained by setting the instrument for the desired wave length and reading the percentage transmittancy direct. The value recorded for each setting represented the average of five readings, among which the greatest variation was not more than 0.5 per cent. By use of reference curves (Figure 1) the concentrations of manganese were read off and the percentage of manganese was calculated. The results are given in Table II.

TABLE I. RESULTS OBTAINED BY VON KNORRE–BISMUTHATE TITRATION METHOD

Bureau of Standards Sample	Type of Steel	Manganese Certificate value	Manganese Found	Difference
		%	%	%
10d	Bessemer, 0.4% C	0.915	0.913	−0.002
13c	B. O. H., 0.6% C	0.700	0.703	+0.003
15a	B. O. H., 0.1% C	0.372	0.363	−0.009
16a	B. O. H., 1% C	0.264	0.266	+0.002
21a	A. O. H., 0.6% C	0.621	0.621	0.000
23a	Bessemer, 0.8% C	0.634	0.638	+0.004
30a	Chrome-vanadium (1.02% Cr, 0.21% V)	0.805	0.813	+0.008
34a	A. O. H., 0.8% C	0.501	0.500	−0.001
35	A. O. H., 1% C	0.300	0.292	−0.008
8c	B. O. H., 0.3% C	0.437	0.439[a]	+0.002
16b	B. O. H., 1% C	0.381	0.381[b]	0.000

[a] Determination made by T. P. Marsh, student at Oregon State College.
[b] Determination made by C. M. Kelley, student at Oregon State College.

TABLE II. RESULTS OBTAINED BY SPECTROPHOTOMETRIC METHOD

(Permanganate solution made up to 1000 ml. and second dilution made as shown when necessary)

Bureau of Standards Sample	Manganese Certificate Value	Solution Diluted to 100 Ml.	Manganese Obtained from Transmittancy at 500 mμ	520 mμ	540 mμ	560 mμ	Average Manganese Found	Difference
	%	Ml.	%	%	%	%	%	%
10d	0.915	50.03	0.908	0.904	0.913	0.912	0.909	−0.006
13c	0.700	50.03	0.699	0.699	0.697	0.699	0.699	−0.001
15a	0.372	None	0.362	0.363	0.361	0.363	0.362	−0.010
16a	0.264	None	0.262	0.262	0.260	0.260	0.261	−0.003
21a	0.621	50.03	0.624	0.619	0.620	0.619	0.621	0.000
23a	0.634	50.03	0.634	0.635	0.635	0.635	0.635	+0.001
30a	0.805	50.03	0.804	0.799	0.804	0.804	0.803	−0.002
34a	0.501	50.03	0.500	0.500	0.500	0.499	0.500	−0.001
35	0.300	None	0.292	0.292	0.291	0.291	0.292	−0.008

PROCEDURE

The procedure is a combination of the von Knorre (*6*) and bismuthate (*9*) methods.

Weigh accurately about 2 grams of sample and transfer to a 500-ml. beaker (tall form preferred). Dissolve in 50 ml. of 1 to 9 sulfuric acid, warming to hasten solution. As soon as the steel has dissolved, dilute to 250 ml., add 10 grams of ammonium persulfate, cover with a watch glass, and boil on the hot plate 10 minutes. If neither pink color nor brown precipitate appears, keep adding small portions of persulfate and boiling. Let cool slightly, add 5 grams more persulfate, and boil 5 minutes. Let cool, add 5 grams more persulfate, and again boil 5 minutes. Let cool, add another 5 grams of persulfate, and boil 10 minutes. Cool to room temperature and filter on a Gooch crucible containing an extra thick pad of asbestos. If the filtrate is not absolutely clear, refilter it through the same pad. Wash the beaker and the residue thoroughly with a 2 per cent solution of ammonium persulfate and finally once with cold water.

Transfer the asbestos pad with the residue to the beaker in which the precipitation was made, cover with water, stir, and add a few millimeters of 1 to 3 nitric acid and just enough solid sodium bisulfite to dissolve all the manganese dioxide. Place the crucible in the beaker and after any adhering precipitate has been dissolved remove and rinse the crucible. Add 50 ml. of 1 to 3 nitric acid, followed by 0.5 gram of sodium bismuthate, and agitate. Let stand 3 minutes, add 50 ml. of 1 to 97 nitric acid, and filter on a Gooch crucible, washing the residue with the same dilute nitric acid (at least 50 ml.) until washings are entirely colorless. Transfer the filtrate to a liter volumetric flask, make up to the mark at 25° C., and mix thoroughly.

By means of the spectrophotometer determine the percentage transmittancy of this solution in a 5-cm. tube at 500, 520, 540, and 560 mμ. If the permanganate solution contains more than 10 mg. of manganese per liter, it will be too opaque for a transmittancy determination and a measured portion of it must be suitably diluted at 25° C. From the respective reference curves read off the milligrams of manganese per liter corresponding to the transmittancies and calculate percentage of manganese for each case, taking into account any extra dilution that was made. Take the average of these values as the percentage of manganese in the sample.

NOTES. 1. All free carbon left when the steel is dissolved is completely oxidized by the persulfate.

2. In dissolving the manganese dioxide by use of bisulfite care must be taken to insure complete solution. Any remaining brownish black particles should be disintegrated with a stirring rod.

3. Removal of the small excess of sulfur dioxide by boiling after the solution of the manganese dioxide is not necessary, since sodium bismuthate oxidizes it along with the manganese.

4. The 1 to 3 and 1 to 97 nitric acid solutions must be free from nitrous acid, which interferes with the bismuthate oxidation (*7*). They are prepared by dilution of concentrated nitric acid which has been boiled for 1 minute, cooled somewhat, and then aërated by suction until perfectly colorless.

Reference Curves

Data for plotting the reference curves were obtained by determining the light transmittancies in a 5-cm. tube at 500, 520, 540, and 560 mμ of a series of solutions prepared by diluting to 250 ml. at 25° C. various volumes of a solution of potassium permanganate that had been standardized against sodium oxalate of known purity. Each transmittancy was determined as soon as the solution had been prepared. Collins and Foster (*2*) state that, since sodium bismuthate oxidizes manganese perfectly to permanganate, a solution of potassium permanganate of known strength is as useful as a manganous sulfate solution for the preparation of standards and that there is no advantage in reducing the permanganate solution and using this reduced manganese for the preparation of standards with nitric acid and sodium bismuthate.

Reference curves (Figure 1) were constructed from the data in Table III by plotting the milligrams of manganese per liter as ordinates against the transmittancies at the given wave length as abscissas. These data are applicable to other spectrophotometers only in case the same values are obtained on similar, known solutions.

TABLE III. DATA FOR CONSTRUCTION OF REFERENCE CURVES

Manganese	Transmittancy at 500 mμ	520 mμ	540 mμ	560 mμ
Mg./l.	%	%	%	%
10.02	4.0	1.0	1.2	5.3
8.91	5.9	1.8	2.0	7.7
8.27	7.4	2.2	2.4	9.2
7.80	8.2	3.0	3.2	10.3
7.37	9.5	3.6	3.8	11.7
7.13	10.1	4.0	4.2	12.3
6.68	12.4	5.0	5.2	14.3
6.24	13.3	5.6	5.8	16.1
6.02	14.1	6.0	6.3	17.0
5.79	15.1	6.9	7.1	18.0
5.57	17.8	7.9	8.4	20.6
5.35	18.3	8.7	9.0	21.1
5.12	19.8	9.2	9.5	22.0
4.92	20.8	10.1	10.5	23.0
4.46	23.7	12.9	13.3	26.0
3.79	27.8	16.8	17.1	31.7
3.34	31.9	21.1	21.7	35.7
2.90	35.8	24.2	25.1	39.9
2.23	47.1	34.1	35.1	49.8

As a further test of the spectrophotometric method, the manganese was determined in two series of solutions of potassium permanganate made by dilutions of a standard solution at 25° C. These results are shown in Table IV. Twenty-three such solutions, in which the manganese concentration ranged from 2.93 to 6.69 mg. per liter, were analyzed with a precision of −0.07 to +0.09 mg. per liter. In six cases there was no deviation from the calculated value.

TABLE IV. RESULTS OBTAINED BY SPECTROPHOTOMETRIC METHOD

Manganese Present	Average Manganese Found	Difference	Manganese Present	Average Manganese Found	Difference
Mg./l.	*Mg./l.*	*Mg.*	*Mg./l.*	*Mg./l.*	*Mg.*
2.93	2.94	+0.01	6.97	6.96	−0.01
3.35	3.31	−0.04	7.25	7.25	0.00
3.63	3.63	0.00	7.66	7.64	−0.02
3.90	3.93	+0.03	8.36	8.44	+0.08
4.18	4.18	0.00	8.64	8.66	+0.02
4.46	4.45	−0.01	4.01	4.00	−0.01
4.74	4.75	+0.01	4.68	4.75	+0.07
5.02	5.02	0.00	5.01	5.01	0.00
5.30	5.28	−0.02	5.35	5.30	−0.05
5.58	5.53	−0.05	6.02	6.02	0.00
6.31	6.40	+0.09	6.69	6.62	−0.07
6.69	6.64	−0.05			

Summary

Manganese can be practically completely separated from iron and the other metals usually occurring in steel by precipitation as hydrated manganese dioxide with excess ammonium persulfate in boiling 1 to 50 sulfuric acid solution.

The spectrophotometric method when carefully carried out is capable of giving results for manganese in steel that are within ±0.01 per cent of the correct value. For manganese in solution the precision is about ±0.1 mg. per liter. Although concentrations of manganese below 2 mg. per liter may be read directly from the curves, it is advisable either to increase the sample weight or to make the permanganate solution up to a volume less than 1 liter that will call for use of the more nearly vertical portion of the curves.

The method may be carried out in a comparatively short time and has the advantage over the colorimetric methods of requiring no color standards. However, it has no advantage over the volumetric bismuthate method; the two methods are to be regarded as alternate procedures.

Acknowledgment

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Determination of Free Silica

Modified Petrographic Immersion Method

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Because of the recent interest in silicosis and the demand for a more rapid method by which the free silica or quartz content may be determined quantitatively in mineral or dust samples, a method has been developed which is reasonably accurate and requires less time than any of the methods in present use.

Free silica may be determined by the chemical method, by the petrographic method, and by a combination of these two methods. In the chemical method (*3*) the separation between free silica and combined silicates is made by treating the powdered specimen with cold hydrofluosilicic acid. The acid dissolves the combined silicates, leaving the free silica. The method requires from 24 to 72 hours, and while reasonably accurate for certain types of minerals, is not satisfactory for others. When compared with petrographic determinations, it is inaccurate for materials such as shale, clay, pumice, etc. Results of analysis of such minerals by the petrographic method correspond much more nearly to the actual facts.

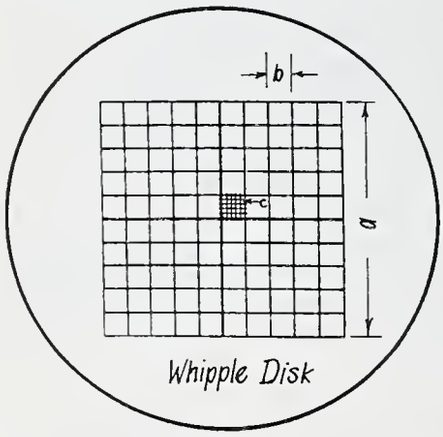

Figure 1

The petrographic method utilizes a polarizing microscope (*1*) by which a thin section of rock specimen is examined. The section is approximately 0.03 mm. in thickness and is mounted in Canada balsam upon a glass slide. Powdered specimens may also be examined in this way, but the grains of powder must be about 0.06 mm. in size. Particles less than 10 microns in size cannot be accurately identified with a polarizing microscope. Various oils are used in which to immerse the grains, depending upon their refractive indices. The Rosiwal method is quantitative and measures the linear intercepts of a given mineral along numerous parallel lines, the percentage of quartz being determined by the ratio between the sum of all of the intercepts of quartz and the length of the measured traverse. A polarizing microscope must be used in this method on rock sections or powders not less than 10 microns in size.

To obtain more accurate results, however, it has been the usual practice to use a combination of the chemical and petrographic methods (*3*). The mineral is treated with an acid and the residue is then examined petrographically to determine whether or not it consists entirely of free silica. If other substances are still present, the acid treatment is continued, in some cases for as long as 72 hours.

Modified Petrographic Immersion Method

In the modified petrographic immersion method, powdered mineral or dust immersed successively in fennel-seed oil and mononitrobenzene is examined with an ordinary microscope equipped with a Whipple disk.

Preparation of Sample. Care should be exercised in the selection and preparation of the sample; only a very small amount of powder is examined and it should be uniform and representative. Rock specimens are crushed, quartered, and ground with an agate mortar and pestle to pass a 150-mesh screen. If the samples are dust taken from ledges, they should not be ground because they are already of the correct size.

Preparation of Slides. A very small amount of ground mineral or dust (approximately 10 mg.) is placed in a 50-cc. beaker and 5 cc. of fennel-seed oil are added and swirled so as to obtain a suspension of the mineral particles in the oil. A similar suspension is made of the ground mineral or dust in mononitrobenzene. A pipet or medicine dropper is used to transfer a sufficient amount of oil-mineral suspension to a Sedgwick-Rafter cell. A cover slip is employed similar to that used in counting dust particles in connection with air-sampling apparatus. In this way two cells are prepared, one containing the pulverized mineral or dust specimen in fennel-seed oil, the other a similar sample in mononitrobenzene. The oil should be the purest obtainable. The mononitrobenzene used by the authors has been rectified. It is well to check a new sample of oil with a pure ground-quartz specimen to verify the refractive index of the oil. Sunlight affects mononitrobenzene and it should be protected against direct rays.

In order to prevent errors, the authors use separate beakers, pipets, and cells for fennel-seed oil and mononitrobenzene, respectively.

The Microscope. An ordinary microscope, meeting the United States Public Health Service specifications for dust counting air samples taken with the Greenberg-Smith impinger (*2*), can be used in this method. The authors use a microscope with a 7.5X eyepiece and a 16-mm. objective, but a higher powered microscope could be used for very fine dusts. The eyepiece is provided with a Whipple disk which has a large square engraved on it covering a large part of the field, the square being divided into medium sized squares, one of these being subdivided further into 25 small squares. As a means of illumination, an ordinary small electric microscope lamp is used.

Microscopic Procedure

After the Sedgwick-Rafter cell has been filled and a cover slip placed over it, being careful to exclude all air bubbles, it is permitted to stand for 30 minutes to allow the dust to settle. It is then placed under the microscope and the objective is raised or lowered until a point is reached where the dust particles are visible. It is not necessary to focus through the entire depth of the liquid, because nearly all the particles will have settled to a single level within 30 minutes. A sufficient amount of the sample is taken to show about 2000 particles on the entire Whipple disk field.

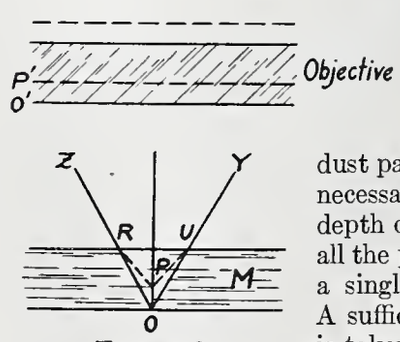

Figure 2

O in Figure 2 represents the definite position of the objective in the case of a particle in focus when nothing but air separates the particle from the objective. Now, if a transparent plate of any medium, *M*, were placed over the particle, between it and the objective, it would be necessary to raise the objective somewhat to bring the object back into focus. This is due to the fact that all rays from *O* are refracted away from the normal on emerging from the transparent plate, as illustrated in Figure 2 by the two rays *ORZ* and *OUY*. In order to bring the particle back into focus, it will then be necessary to raise the objective through the distance *OP* or *O'P'*.

Since nearly all the particles of minerals or dusts are thinner

on the edge than in the center, when they are immersed in liquids they act as imperfect lenses (*4*) to refract the light, provided they differ in index of refraction from the liquid. If the particle has a higher index than the liquid, it tends to bring light to the focus above the fragment. Therefore, a slight raising of the objective from good focus on the particle causes brightness or transparency within the area of the particle. As the microscope tube is raised higher above focus, this bright area contracts and becomes brighter or more transparent. If the tube is lowered below focus, the particle appears darker than the rest of the field and a highly illuminated halo may surround it. As the tube is lowered, this halo moves outward from the particle. If the mineral has a lower index of refraction than the liquid, it brings light to a focus below the particle. Therefore, a slight lowering of the objective from good focus on the particle causes brightness or transparency within the fragment, and conversely a slight raising above good focus causes the particle to darken.

Quartz or free silica has a definite index of refraction—1.544. Certain minerals have higher and others have lower indices of refraction. If we immerse dust consisting of quartz and minerals of lower and higher refractive indices than quartz in fennel-seed oil which has a refractive index of 1.540, focus the microscope, and then slightly raise the objective above this point of good focus, several particles appear lighter than the surrounding medium while the remainder appear darker. The bright or transparent particles will consist of quartz plus particles which have a higher refractive index than quartz. Similarly, if we immerse another portion of the same dust in mononitrobenzene, which has a refractive index of 1.55, some of the particles appear brighter than the surrounding medium when we raise the objective slightly above the point of good focus. This time, however, the bright or transparent particles are only those which have a higher refractive index than quartz. Therefore, if we call the percentage of transparent particles in fennel-seed oil A and the percentage of transparent particles in mononitrobenzene B we have:

$$A - B = \text{per cent quartz or free silica}^{1}$$

However, as quantitative results are desired, it is necessary not only to count the number of particles but to apportion to each particle its due weight, depending upon its size. The authors have divided the particles into two unit sizes, the first including those particles having an area of less than one-tenth the area of the smallest division on the Whipple disk. These units are given a weight of 1. The second grouping includes all the larger particles which are divided into 10-units, each 10-unit being given a weight of 10. A particle having an area of one-tenth of the smallest division on the Whipple disk is called one 10-unit with a weight of 10. The entire area of the smallest division on the disk (*c*, Figure 1) is given a weight of 100 or ten 10-units. A particle having one-half the area of the smallest square on the disk is given a weight of 50 or five 10-units. The authors have found it simpler and more rapid if the larger particles are counted first in units of ten, then counting the 1-unit particles. The weight of transparent particles is then obtained in the following manner:

$$\text{No. of transparent 10-size units} \times 10 = A$$
$$\text{No. of transparent 1-size particles} \times 1 = B$$
$$A + B = \text{weight of transparent particles}$$

The objective is then lowered until all the particles are in good focus and the procedure outlined above is followed, this time counting and weighting all particles, both light and dark, in order to determine the total particle weight.

$$\text{Total number of 10-size units} \times 10 = C$$
$$\text{Total number of 1-size particles} \times 1 = D$$
$$C + D = \text{total weight of all particles}$$

Then

$$\frac{A + B}{C + D} = \text{per cent of transparent particles}$$

This procedure is followed with both the fennel-seed oil cell and the mononitrobenzene cell. In fennel-seed oil the transparent particles represent quartz and also those minerals having a higher index of refraction than quartz. The transparent particles in mononitrobenzene represent only minerals having a higher index of refraction than quartz. We then have:

Per cent of transparent particles in fennel-seed oil minus per cent of transparent particles in mononitrobenzene equals per cent of free silica

Any slight error made in counting and weighting these particles is self-compensating and good checks can be obtained.

It will be of considerable assistance if the chemist in familiarizing himself with this method prepares a sample of material high in free silica, such as a pure silica sand, and another mineral, such as pumice, containing practically no free silica, and examines them under the microscope to accustom his eye to the changes occurring when the objective is raised or lowered. The authors have found it more accurate and quicker in some cases to count and weight the particles which darken when the objective is raised, the percentage of transparent particles being found by difference. Very often the silica particles in mononitrobenzene appear to have a yellowish tinge, but this is not always the case and the authors hesitate to recommend this color change as a qualitative means of identifying free silica.

It has been found helpful to use a hand tally or counter in making these counts. To insure greater accuracy, it is important to examine several fields on a cell and count an area which appears to be representative. The entire field covered by the Whipple disk is usually counted.

Blanks should be run to correct for any dust particles which might be contained in the oils or on the Whipple disk, etc., and this number of dust particles subtracted from counts in each case. Most of these dust particles can be recognized because they remain in the field as the position of the objective is changed, and should not be counted.

Table I. Refractive Indices of Oils

Number	Index	Liquid	Number	Index	Liquid
1	1.33	Water	12	1.56	Monobromobenzene (1.578— beta-sericite)
2	1.36	Ethyl alcohol			
3	1.44	Chloroform	13	1.59	Bromoform
4	1.47	Glycerol	14	1.60	Cassia oil
5	1.48	Castor oil	15	1.62	Monoiodobenzene
6	1.49	Xylene	16	1.64	Monochloronaphthalene (alpha)
7	1.50	Benzene			
8	1.51	Cedar oil	17	1.66	Monobromonaphthalene (alpha)
9	1.53	Clove oil			
10	1.54	Fennel-seed oil (1.544—quartz)	18	1.70	Cadmium borotungstate
11	1.55	Mononitrobenzene	19	1.74	Methylene iodide

Where the technician has difficulty in distinguishing between dark and light particles, as may sometimes occur, especially in the case of beginners, it is helpful to raise the objective considerably higher than usual. In this way the light particles drop out of vision and the dark particles remain dark and are more readily identified. The size of these dark particles can then be determined by lowering the objective to the normal position. The small division *c* on the Whipple disk (Figure 1) should be referred to constantly in order to gage the size of the particles accurately. Rapid raising and lowering of the objective increase the apparent contrast between the transparent and dark particles, and by this means particles may be more positively identified.

Although fennel-seed oil and mononitrobenzene were used by the writers, other liquids having similar refractive indices may be used.

In some cases this method is very rapid. If a mineral such as spodumene is prepared and immersed in mononitrobenzene and all the particles appear transparent when the objective is raised, the sample contains no quartz. If some particles remain dark when the objective is raised and do not become transparent when the objective is lowered below focus, the sample may also be considered to be free from quartz. The reverse is true in fennel-seed oil. If there are no bright particles when the objective is raised as in the case of pumice, the sample contains no quartz or minerals of a higher refractive index.

[1] This method does not positively identify the counted particles as quartz. There are other minerals whose refractive indices would fall within the limits 1.54 to 1.55. But in ordinary dust analyses these other minerals do not occur in amounts sufficient to cause appreciable error.

Table II. Comparison of Results by Chemical and Modified Petrographic Immersion Methods

Kind of Sample	Chemical Method	Petrographic Immersion Method	Difference
	%	%	%
Dust from ledge next to furnace of brass foundry	36.8	35.5	+1.3
Another dust sample from different ledge of same foundry	51.2	46.9	−4.3[a]
Parting compound	2.9	3.4	+0.5
Silica sand	99.6	96.6	−3.0
Emery-wheel dust	6.1	2.3	−3.8[a]
Portland cement	0.6	1.3	+0.7
Tripoli	91.3	95.1	+3.8
Limestone	5.6	5.8	+0.2
Dust from center of annealing room of iron foundry	34.3	35.8	+1.5
Dust from ledge of iron foundry	61.8	59.6	−2.2[a]
Dust from ledge of iron foundry	63.1	58.0	−5.1[a]
Dust from center of steel foundry near electric furnace	52.1	46.7	−5.4[a]
Dust next to portable grinders in iron foundry	2.6	4.6	+2.0
Dust from platform at rotary facing and coarse sand mixer of iron foundry	60.5	60.2	−0.3
Dust from center of dry tumbling room of iron foundry	47.1	45.4	−1.7
Dust in front of grinding wheels in iron foundry	22.4	23.5	+1.1
Dust in front of sand-blast barrels of iron foundry	61.1	53.7	−6.4[a]
MATERIALS CONTAINING AN APPRECIABLE AMOUNT OF COMBINED SILICA			
Shale used in brick works	37.9	1.1	−26.8[a]
Shale and clay used in brick works	48.1	0.9	−47.2[a]
Clay for lining ditches	35.0	1.7	−33.3[a]
Frit for enameling	27.1	13.5	−13.6[a]
Rock borings from schist	20.2	13.5	−6.7[a]
Trap rock	16.8	17.3	+0.5
Fuller's earth	44.3	0.8	−43.8[a]
Granite No. 1	55.1	34.2	−21.9[a]
Feldspar (commercial orthoclase)	31.1	28.2	−2.9[a]
Glass	19.6	0	−19.6[a]

[a] Results obtained in tests where there was an appreciable amount of residue in the platinum crucible after hydrofluorization. These residues indicate that combined silicates were present and that the results by the chemical method are too high.

The writers believe this quantitative method can be utilized for the determination of other nonopaque mineral compositions such as fluorite, beryl, etc., using oils with the correct refractive indices. To aid other investigators, a list of oils is given in Table I taken from "Elements of Optical Mineralogy" by Winchell (*5*). These oils were selected so that those adjacent in the list are miscible and they may be mixed to obtain any intermediate refractive index.

Table III. Triplicate Silica Determinations by Modified Immersion Method

Kind of Sample	First Trial	Second Trial	Third Trial	Greatest Deviation	Average Deviation
	%	%	%	%	%
Dust from ledge next to furnace in brass foundry	37.1	36.5	32.9	4.2	1.7
Parting compound	3.5	3.7	3.1	0.6	0.2
Silica sand	97.4	95.9	96.6	1.5	0.5
Dust from ledge of shakeout room in brass foundry	49.3	46.7	44.8	4.5	1.6
Emery-wheel dust	1.9	2.2	2.6	0.7	0.3
Portland cement	1.0	1.6	1.4	0.6	0.3
Tripoli	93.3	94.9	97.1	3.8	1.4
Frit	13.5	12.3	11.4	2.1	0.7
Rock borings from schist	12.2	13.5	13.4	1.3	0.5
Shale used in brick works	1.1	0.9	1.3	0.4	0.1
Glass	0	0	0	0	0
Bastard rock (limestone)	5.8	6.3	5.4	0.5	0.3
Trap rock	16.6	19.0	16.3	2.7	1.3
Fuller's earth	0.9	0.7	0.8	0.1	0.1
Granite No. 1	33.7	33.9	34.9	1.2	0.5
Dust from center of annealing room of iron foundry	34.5	35.2	37.4	2.9	1.1
Dust from ledge of iron foundry	60.5	57.5	60.8	3.3	1.3
Dust from ledge of iron foundry	60.4	59.6	58.8	1.6	0.5
Dust from center of steel foundry near electric furnace	47.9	45.6	46.5	2.3	0.8
Dust next to portable grinders in iron foundry	4.1	4.7	5.0	0.9	0.3
Dust from platform of mixer in iron foundry	59.4	61.0	60.2	1.6	0.5
Dust from center of dry tumbling room of iron foundry	44.2	47.0	45.0	2.8	1.1
Dust in front of grinding wheels in iron foundry	23.8	23.9	22.8	1.0	0.5
Dust in front of sand-blast barrels	54.7	52.3	54.1	2.4	0.9
Feldspar (commercial orthoclase)	28.7	27.9	28.0	0.8	0.3

Table II shows comparison of the results obtained by the chemical and modified petrographic immersion methods. In the chemical method, the samples were immersed for 24 hours in hydrofluosilicic acid. For samples containing considerable combined silicates, such as pumice, clay, shale, etc., 24-hour immersion is not sufficient. The first seventeen samples contain only small amounts of combined silicates, whereas the remainder are high in combined silicates, showing the error introduced by the chemical method unless sufficient time is allowed for immersion of the sample in hydrofluosilicic acid.

Table III gives the results by the modified immersion petrographic method and shows the excellent checks obtained on the same sample by the same chemical engineer. The first ten samples were run on one-quarter of the Whipple disk, whereas on the remaining samples the entire field of the Whipple disk was counted. Counting the entire field increased the accuracy considerably.

In order that the accuracy of the method might be definitely determined, sample mixtures were made by thoroughly mixing known amounts of pure quartz with pumice, with glass, and with pumice and spodumene. (Blanks were run to determine their purity.) The results are shown in Table IV.

Table IV. Tests of Sample Mixtures

Sample	Free Silica Actually in Sample	Free Silica Found: Modified petrographic immersion method	Free Silica Found: Chemical method, 72-hour immersion
	%	%	%
Mixture of pure quartz and pumice	9.9	10.1	29.8
Mixture of pure quartz and glass	33.2	32.9	44.5
Mixture of pure quartz and spodumene	69.6	69.1	63.3

Conclusions

The writers believe the method is reasonably accurate. With practice it can be used by any chemist.

It is more rapid than other methods now used, a final result being obtainable in about one hour's time, including preparation of sample but excluding the half hour during which the sample is allowed to stand before the count is made.

The method is especially useful for the examination of dusts which have been deposited on ledges and beams, most of the particles being less than 10 microns in size.

No special equipment is required, other than that used in making microscopic dust counts according to the United States Public Health Service method.

The examination can be made in the field, if desired.

Acknowledgment

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Determination of Minute Amounts of Lead in Biological Materials

A Titrimetric-Extraction Method

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A method sensitive to 0.001 mg. is described for the determination of minute amounts of lead in biological materials. Dithizone (diphenylthiocarbazone) is employed first in the separation of the lead from other metals, and secondly in the final estimation of the lead by means of a quantitative titrimetric extraction. Bismuth is the only interfering element likely to be encountered. A series of 10- to 15-gram samples of whole blood can be analyzed with an average time per sample of about 2 hours.

In connection with an investigation concerning the efficacy of various colloidal lead preparations for the treatment of certain diseases, a procedure for the quantitative determination of minute amounts of lead in blood, excreta, tissues, etc., was required. A review of the literature indicated the necessity for a method sensitive to 0.001 mg. of lead. Of the numerous methods proposed, those considered most promising were studied principally with respect to lead recovery and to the sensitivity of the final reaction by means of which lead estimation is made.

The radio-indicator technic (*12*), with either radium-D or thorium-B, was employed for the purpose of ascertaining lead losses. Despite numerous refinements in technic, chromate methods (*7, 11, 14, 16*), colorimetric lead sulfide methods (*2, 10, 18, 23*), the turbidimetric metabisulfite procedure (*4, 6, 13, 18*), and electrolytic methods (*3, 12, 15, 17, 20, 22, 24*) were all unsatisfactory in the authors' hands. The most promising line of attack was found to be the reaction between lead and dithizone (diphenylthiocarbazone), which has received considerable study, particularly by Fischer and his co-workers (*8, 9*), either as a means for preliminary lead separation, or for both this and subsequent lead estimation. Their investigations have served as the basis for further work by others (*1, 5, 19, 21, 25*). Fischer and Leopoldi (*9*) state that dithizone may be used for the separation of minute amounts of lead from relatively large quantities of aluminum, antimony, arsenic, beryllium, cadmium, copper, mercury, silver, and zinc. Bismuth, monovalent thallium, and stannous tin are interfering elements. The colorimetric procedure of Fischer and Leopoldi (*9*) was evaluated but was found unsatisfactory because of the large number of standards required to cover a wide range of lead values, the instability of these standards, and the nonreproducibility of color both in standards and samples.

During this investigation it was observed that lead can be quantitatively extracted with a dithizone solution without using an appreciable amount of excess reagent. This observation led to the development of what may be called a titrimetric-extraction method for estimating lead. In this method, initial lead separation is made with a chloroform solution of dithizone, the lead is converted to the nitrate, and it is then reëxtracted with the least possible amount of a standardized dithizone solution. A reagent blank is carried along simultaneously with the sample, and proper correction is made for lead added in this manner. The use of dithizone simplifies the analytical procedure by reducing the number of steps involved, thereby minimizing the chances for lead losses and lead contamination.

The method is described below in terms of the procedure used for the analysis of 10- to 15-gram samples of whole blood. It is also applicable in the analysis of tissue, bone, and excreta, as well as larger amounts of blood, the only modification being that larger quantities of reagents are required for the destruction of organic matter and for the preparation of the digestion residue for dithizone extraction.

Procedure

Glassware and Reagents. Pyrex glassware should be used wherever possible. Consistent results cannot be obtained with ordinary resistance-glass digestion flasks or separatory funnels. The separatory funnels should preferably be of the Squibb type. It is absolutely necessary that each piece of glassware used be scrupulously clean. Immediately before use, the article, previously cleaned by conventional methods, is further cleaned with a mixture of a dilute solution of potassium cyanide and dithizone solution No. 2. If the piece of equipment shows a negative lead test, it is again thoroughly rinsed with redistilled water and is then ready for use.

The reagents should be as free from lead as possible, but it is not necessary to purify the best c. p. grades of these materials. Combined reagent blanks are carried along simultaneously with each analysis and the results are corrected accordingly. The concentrations of ordinary reagents are expressed on a volume per cent basis, referred to the usual commercial concentration; thus, 5 per cent ammonium hydroxide contains 5 ml. of ammonium hydroxide (sp. gr. 0.90) in 100 ml. of solution. The special reagents required are as follows:

1. Citric acid solution, 4 per cent: 40 grams of the monohydrate and 1 gram of salicylic acid (as preservative) per liter of solution.
2. Sodium chloride-hydrochloric acid solution: 5 per cent hydrochloric acid saturated with sodium chloride at room temperature.
3. Redistilled water. Water distilled from a large Barnstead still is redistilled from alkaline permanganate solution in an all-glass Pyrex still. This double-distilled water is used in all cases except for preliminary rinsing in cleaning operations.
4. Dithizone solution No. 1. Dithizone was obtained from the British Drug Houses, Ltd., London, England. This material is quite impure, but for the initial separation of lead it may be used without purification. A solution is prepared for this purpose containing 0.04 gram of the impure dithizone per liter of chloroform.
5. Dithizone solution No. 2. The dithizone used in the titrimetric extraction must be purified. One-tenth gram of the commercial material is dissolved in 30 ml. of chloroform in a large separatory funnel, and the solution is extracted once with 900 ml. of 0.5 per cent ammonium hydroxide solution. After discarding the chloroform phase, the aqueous phase is neutralized to litmus with 10 per cent hydrochloric acid, and the purified dithizone thus precipitated is extracted with chloroform. The chloroform solution is then diluted so as to be equivalent to 0.01 mg. of lead per ml. (about 1400 ml., depending on the purity of the initial material). The solution is delivered to a Pyrex reservoir from which siphons lead to a series of burets. The stopcocks in the

delivery system and in the burets are lubricated with glycerol. A very small amount of Lubriseal is used at the extreme ends of each stopcock. Both the supply reservoir and the burets are suitably protected against evaporation of chloroform and undue exposure to light.

Standardization. Dithizone solution No. 2 is standardized in the following manner:

Five to 20 ml. of a standard solution of recrystallized lead nitrate containing 0.01 mg. of lead per ml. are delivered to a 125-ml. separatory funnel. If less than 20 ml. are taken, the volume is made up to 20 ml. with water. After the addition of 2 ml. of 10 per cent potassium cyanide solution and 2 to 3 drops of phenol red, the solution is adjusted to pH 7.5 with 5 per cent nitric acid. If 0.20 mg. of lead is taken for standardization, 10 ml. of the dithizone solution are delivered from a buret to the separatory funnel, which is then vigorously shaken. The green color of the reagent solution is immediately discharged with the simultaneous formation of the brilliant reddish orange colored lead-dithizone complex, which is soluble in the chloroform but practically insoluble in the aqueous phase. Shaking is continued until no further increase in the depth of color is produced, indicating that the reaction is substantially complete. A mechanical shaker greatly facilitates the work. After complete subsidence, the chloroform layer is discarded, 5 ml. of the dithizone solution are added to the separatory funnel, and the extraction procedure is repeated. (About 0.10 ml. of the chloroform phase is left in the separatory funnel after each extraction to prevent any loss of the aqueous phase.) This is continued, using smaller and smaller quantities of the dithizone solution, and removing each chloroform extract before the next portion of dithizone is added.

As the end point is approached, the dithizone reagent is added in 0.1-ml. and finally 0.05-ml. portions, a few drops of chloroform being added to give an adequate volume for judging the color produced. A stage is eventually reached where the green color of the added increment of reagent changes to a purple shade that persists after vigorous and prolonged agitation. The next 0.05-ml. addition of dithizone should remain practically unchanged in color. This green stage is taken as the end point, and the total volume of dithizone solution consumed up to that point is read from the buret. A blank determination, in which 20 ml. of water are used in place of the lead nitrate solution, is carried through in exactly the same way as the sample. After deduction of the blank correction, the lead equivalence of the reagent solution is calculated. Because of gradual deterioration, this solution must be standardized on each day analyses are made.

Preparation of Sample. The organic matter in 10 to 15 grams of whole blood is completely destroyed by wet oxidation in a Kjeldahl flask wherein 15 ml. of concentrated nitric acid (sp. gr. 1.42), 2 ml. of concentrated sulfuric acid (sp. gr. 1.84), and 2 ml. of perchloric acid (sp. gr. 1.54) are used, and are added in this order.

After adding the nitric acid, the digest is concentrated to somewhat less than 5 ml. The sulfuric acid is then added and heating at the same temperature is continued until the nitrogen oxides have been completely driven off. Following this, the temperature is increased until sulfur trioxide fumes are evolved, and shortly afterwards the perchloric acid addition is made. The function of the perchloric acid is to oxidize rapidly and completely the remaining organic matter. This reagent is not dangerous to use for this purpose, provided it is added dropwise to the hot, fuming digestion residue. After the addition of the perchloric acid, the fuming off of sulfur trioxide is continued for about 5 minutes. The final volume is about 3 ml. Whereas the use of 0.05 gram of lead-free selenium as a catalyst is definitely advantageous in the digestion of 50 to 100 grams of whole blood, it does not noticeably shorten the time required for this operation in the case of 10- to 15-gram samples.

To the cooled digest 5 ml. of water are added and the residue is dissolved by the addition of 5 ml. of the sodium chloride–hydrochloric acid solution, with subsequent heating. The solution is then made just barely alkaline to litmus with ammonium hydroxide (sp. gr. 0.90), after which 5 ml. of 4 per cent citric acid solution are added to dissolve the precipitated ferric hydroxide. Gentle heating is conducive to complete solution, which must be obtained at this stage. Two milliliters of 10 per cent potassium cyanide solution are added, followed by ammonium hydroxide (sp. gr. 0.90) until the solution is just alkaline to litmus, and then by 1 to 2 additional drops. The solution is now transferred from the Kjeldahl flask, with thorough rinsing with water, to a 250-ml. separatory funnel.

Separation of Lead. The separation of lead (and bismuth, if present) from other metals is effected by extraction of the sample, prepared as described above, with dithizone solution No. 1.

In order to insure the complete removal of lead from the Kjeldahl flask, a drop of 10 per cent potassium cyanide solution, 0.5 ml. of water, and the first 5 ml. of dithizone solution No. 1 to be used in the extraction procedure, are added to the flask, vigorously shaken, and then quantitatively delivered, with thorough rinsing with water, to the 250-ml. separatory funnel containing the sample.

The separatory funnel is shaken, and, depending upon the amount of lead present, the color of the chloroform layer ranges from a brilliant red-orange, with appreciable amounts of lead, through purple to the unchanged green color of the dithizone reagent solution. Extraction of the aqueous solution is repeated with successive 5-ml. portions of the dithizone solution, delivering each, after extraction, to a 125-ml. separatory funnel, until the color of a newly added portion of dithizone remains unchanged. The aqueous phase is extracted once more, as a precautionary measure, and is then discarded. The total volume of dithizone solution used is noted as it gives a preliminary indication of the amount of lead present and is therefore of value as a guide in the final lead estimation.

The chloroform solution of the lead-dithizone complex is first washed with 25 ml. of water containing one drop of 10 per cent potassium cyanide solution, quantitatively separated, and transferred to another 125-ml. separatory funnel. Contamination of either phase by the other is avoided by running out the chloroform layer until about 0.2 ml. remains. Small portions of chloroform are successively added and withdrawn, maintaining a chloroform trap at all times, until the separation of all chloroform-soluble components is complete. The lead is removed from the organic complex by shaking the chloroform solution with 10 ml. of 1 per cent nitric acid; the dithizone remains in the chloroform phase, whereas the lead, in the form of the nitrate, passes into the aqueous phase.

After separation of the two phases, the lead nitrate solution is washed once with chloroform. The chloroform solution containing the bulk of the dithizone and the chloroform wash are combined and reëxtracted with a second 10-ml. portion of 1 per cent nitric acid. After separating and washing this aqueous phase as before, it is added to the first lead nitrate solution, and the combined solution is washed repeatedly with small portions of chloroform until a freshly added portion remains colorless. The lead nitrate solution is now ready to be prepared for the final titrimetric extraction. If the initial dithizone extraction indicated the presence of more than 0.2 mg. of lead, the sample is diluted to a known volume and an aliquot is taken for final analysis. Samples containing up to 0.50 mg. can be handled satisfactorily, in which case the extracting reagent is standardized against a corresponding known amount of lead. It is more convenient, however, to work with 0.20 mg. of lead or less.

The sample is prepared for the final extraction by adding 2 ml. of 10 per cent potassium cyanide solution, 2 to 3 drops of phenol red, and then 5 per cent ammonium hydroxide dropwise until pH 7.5 is reached.

Lead Estimation by Titrimetric Extraction. The titrimetric extraction of the lead is carried out with dithizone solution No. 2 in exactly the same manner as used for the standardization of this reagent. From 15 to 25 per cent of the total volume of dithizone estimated to be required is used in the first step of the extraction, which is then continued, using smaller and smaller portions of the dithizone solution, as previously described. Combined reagent blanks, consisting of the same amounts of all the reagents as used in the analysis, are carried along simultaneously with the sample and in identical apparatus.

If the end point should be overstepped, a reëxtraction can be made, provided all the lead-dithizone extracts of the sample have been saved. The chloroform solution is extracted twice with 1 per cent nitric acid and the resulting lead nitrate solution is again prepared for titrimetric extraction in exactly the same manner as previously described.

Experimental Results

The accuracy of the method is illustrated by the following representative results. The data in Table I were obtained

during the preliminary testing of the titrimetric-extraction procedure when applied directly to pure solutions of lead chloride and lead nitrate.

Table I. Determination of Lead in the Absence of Other Metals

Lead Taken	Lead Found	Error
Mg.	*Mg.*	*Mg.*
As $PbCl_2$		
0.500	0.500	0.000
0.500	0.500	0.000
0.200	0.199	−0.001
0.100	0.100	0.000
0.100	0.101	+0.001
0.100	0.100	0.000
As $Pb(NO_3)_2$		
0.100	0.100	0.000
0.050	0.051	+0.001
0.050	0.049	−0.001
0.050	0.051	+0.001
0.010	0.010	0.000

In developing this procedure for the analysis of whole blood, numerous attempts were made under various conditions to apply the titrimetric extraction immediately after destruction of the organic matter. A way to avoid the oxidation of the dithizone reagent by ferric iron in the presence of potassium cyanide could not, however, be found. Recourse was then had to a preliminary dithizone extraction for separating the lead, in which the partial destruction of the reagent is of no importance, after which the titrimetric extraction can be made without interference. Table II indicates the completeness with which lead is separated from relatively large amounts of iron by using this double-extraction procedure.

Table II. Determination of Lead in the Presence of 1.0 Gram of Iron as Ferric Sulfate

Lead Added	Total Lead Found	Added Lead Recovered	Error
Mg.	*Mg.*	*Mg.*	*Mg.*
0.100	0.152	0.099	−0.001
0.100	0.154	0.101	+0.001
None	0.052 } Blanks	...	....
None	0.053 }		

In these experiments the lead, in the form of nitrate, was added to ferric sulfate, and after the addition of 2 ml. of concentrated sulfuric acid (sp. gr. 1.84) the solution was evaporated to copious fumes of sulfur trioxide. After cooling, 50 ml. of water and 10 grams of citric acid were added, the latter for the purpose of preventing the precipitation of iron when the solution was subsequently made alkaline. Equally good lead recoveries were obtained in another series of experiments in which amounts of lead, as the nitrate, ranging from 0.1 to 0.5 mg., were added to samples of 0.10 gram of iron as ferric nitrate. In each instance 2 grams of citric acid were added, the alkalinity of the solution was properly adjusted, and the sample then handled by the double-extraction procedure. This finding is at variance with the statement of Allport and Skrimshire (*1*) that nitrates interfere with the complete extraction of lead, particularly in the presence of a large proportion of iron.

The results in Table III represent a few of the tests performed upon leaded blood specimens during the preliminary development of the method. Experience with the technic has enabled similar analyses to be made with a substantially consistent error not exceeding ±0.001 mg. of lead. The analyses made on the 15-gram blood samples are particularly interesting in that three analysts collaborated, each working independently of the others.

Discussion

It is important that the digestion residue be completely dissolved before attempting initial lead separation, since otherwise lead adsorption, with resultant lead loss, is likely to occur. The sodium chloride–hydrochloric acid solution not only is an excellent solvent for lead sulfate, but has also dissolved all other residues remaining after digestion. Some of these were resistant to citric acid and/or ammonium citrate, even upon prolonged heating.

In carrying through the titrimetric extraction, equilibrium in the distribution of lead between the aqueous and chloroform phases must be attained with each portion of dithizone solution before continuing to the next. Otherwise erroneous results will be obtained, and near the end point a series of pinkish purple shades will be obtained instead of the distinct and abrupt changes through the colors light pink, purple, and green, with the last three 0.05-ml. additions of dithizone solution. Since dithizone is soluble in alkaline aqueous media, the pH of each solution just before titrimetric extraction must be carefully adjusted to the same value. Consistent results are obtainable by controlling the dithizone distribution between the aqueous and the chloroform phases in this way. Extensive tests have shown that the method is equally accurate at pH values higher than 7.5—e. g., pH 8.4 to 9.0. The latter pH may not be the upper limit of the working range. The important factor in this connection is that both sample and blank must be adjusted to the same pH.

Table III. Determination of Added Lead in Beef Blood

(In these experiments the lead, as lead nitrate, was added by another chemist in amounts unknown to the analysts.)

Lead Added	Total Lead Found	Added Lead Recovered	Error
Mg.	*Mg.*	*Mg.*	*Mg.*
	100-gram blood samples		
0.210	0.247	0.207	−0.003
0.200	0.241	0.201	+0.001
0.110	0.148	0.108	−0.002
0.100	0.140	0.100	0.000
0.050	0.093	0.053	+0.003
0.050	0.086	0.046	−0.004
0.011	0.051	0.011	0.000
None	0.040 } Blanks	...	....
None	0.040 }		
0.008	0.036	0.007	−0.001
0.010	0.038	0.009	−0.001
0.010	0.039	0.010	0.000
None	0.028 } Blanks	...	....
None	0.029 }		
	50-gram blood samples		
0.115	0.135	0.116	+0.001
0.077	0.100	0.081	+0.004
0.045	0.065	0.046	+0.001
None	0.019 Blank	...	....
	15-gram blood samples		
0.004[a]	0.024	0.005	+0.001
0.004[b]	0.021	0.004	0.000
0.055[a]	0.076	0.057	+0.002
0.055[b]	0.073	0.056	+0.001
0.055[c]	0.073	0.054	−0.001
None[a]	0.019 } Blanks	...	....
None[b]	0.017 }		
None[c]	0.019 }		

[a] Analyst F.
[b] Analyst E.
[c] Analyst C.

Unless constant care is exercised throughout the entire procedure to avoid lead contamination, consistent accuracy cannot be obtained. A likely source of contamination is in the handling of the separatory funnels. The authors have found it distinctly advantageous to wire the stopper to the neck of the separatory funnel with a loose loop of copper wire, which permits easy removal of the stopper but does not allow it to hang in contact with the sides of the funnel. The ground-glass surface must not come in contact with the fingers or other contaminants. Whereas it is preferable not to lubricate the stopper—the water seal is entirely satisfactory—the stopcock may be coated with a thin film of Lubriseal. Once a separatory funnel has been brought into active use, it is protected from dust, fumes, etc., between analyses. Before being used again it is only necessary to wash with dilute nitric acid and then test with dithizone solution No. 2 as described under "Glassware and Reagents," to insure the complete absence of lead contamination.

In the experimental work reported above, bismuth was considered the only interfering element likely to be present. If the beef blood used in this study contained bismuth, it is apparent that it did not interfere with the satisfactory recovery of added lead. Experimentation is now under way

to extend the applicability of the method to biological materials containing bismuth.

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Selenite-Phosphate Method for Determining Zirconium in Ores

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THE selenite method has been shown to be capable of giving accurate results and to be applicable to the determination of zirconium in ores (*3*) and in alloys (*1*). It is somewhat longer than the phosphate method, but the freshly precipitated zirconium selenite is soluble in hydrochloric acid and errors of co-precipitation can be readily eliminated by a second precipitation before ignition to the oxide.

A combination of the two methods would seem to have certain advantages over either method alone: over the phosphate method, in that two independent precipitations of the zirconium can be made easily without resort to intermediate fusion, and the effect of co-precipitation can thus be made negligible; over the plain selenite method, in a shortening in the time of analysis without appreciable sacrifice of accuracy. Such a combination method has been found applicable to the determination of zirconium in steels (*2*). When applied to ores, it would be particularly advantageous where thorium is present. Thorium, when present alone, is unprecipitated by either phosphate or selenite under proper acid concentrations, but it is very badly co-precipitated by either method when present with zirconium. Previous removal of thorium as oxalate in the selenite method was found to require several extra steps to bring the solution to a state suitable for the precipitation of zirconium selenite, but these would not be necessary if thorium were removed following a selenite precipitation and prior to a phosphate precipitation, for the sulfuric acid used to destroy the excess oxalate serves as the proper medium for the precipitation of zirconium phosphate.

Decompose the ore and precipitate the zirconium once as in the plain selenite method (*3*). If thorium is present, dissolve the precipitate in a mixture of 40 cc. of 10 per cent oxalic acid solution and 12 cc. of 6 *N* hydrochloric acid. Filter off the thorium oxalate and destroy the excess oxalate by evaporation with 50 cc. of 18 *N* sulfuric acid, as in the selenite method. If thorium is absent, dissolve the zirconium selenite precipitate in 50 cc. of 18 *N* sulfuric acid. In either case dilute the sulfuric acid solution to 200 cc. and filter off any precipitated selenium. If a small amount of red selenium runs through the paper it may be neglected. Heat the solution to 50° C., and add 20 cc. of 3 per cent hydrogen peroxide and 50 cc. of a 20 per cent solution of diammonium phosphate, precipitating zirconium phosphate. Allow to stand 2 hours, filter, wash thoroughly with a 5 per cent solution of ammonium nitrate, and ignite slowly. Gradually raise the temperature to the full heat of the Tirrill burner and weigh as ZrP_2O_7.

The reproducibility of the method is illustrated by the analysis of zirconium concentrates which gave the following values for the percentage of ZrO_2 present: 50.88, 51.10, 50.87, and 50.50; average, 50.84.

When applied to samples of ores, the method was found to be rapid and accurate. Results obtained on samples made by mixing known amounts of zirconium dioxide with varying amounts of feldspar, apatite, thoria, etc., are shown in Table I.

Table I. Analysis of Artificial Zirconium Ores by the Selenite-Phosphate Method

	Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
ZrO_2	0.1103	0.1185	0.1007	0.1221	0.1225	0.1028
Feldspar	0.30	0.25	0.20	0.20	0.15	0.15
Apatite	0.10	0.10	0.050	0.050	0.050	0.050
ThO_2	....	0.050	0.050	....	0.050	0.050
TiO_2	....	....	0.050	0.050	0.050	0.050
NH_4VO_3	....	....	....	0.050	0.050	0.050
CeO_2	....	....	....	....	0.050	0.050
Sample	0.5106	0.5208	0.4520	0.4720	0.5230	0.5010
ZrP_2O_7 found	0.2355	0.2551	0.2160	0.2640	0.2656	0.2224
ZrO_2 calcd.	0.1093	0.1184	0.1003	0.1226	0.1233	0.1033
	%	%	%	%	%	%
ZrO_2 present	21.60	22.76	22.25	25.89	23.42	20.51
ZrO_2 found	21.42	22.75	22.19	25.99	23.58	20.62

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Confining Liquids for Gas Analysis

Solubility of Carbon Dioxide in Salt Solutions

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THE use of mercury as a confining liquid in the buret for gas analysis is recognized as best practice for accurate work, as all common gases analyzed in the usual apparatus are insoluble in and do not react with mercury. However, the cost and great density of mercury are two disadvantages that make it common practice to substitute an aqueous solution for mercury in routine work.

The two most commonly used confining solutions are saturated sodium chloride with 2 volume per cent hydrochloric acid, and 20 per cent sodium sulfate with 5 volume per cent sulfuric acid, the solutions being colored with methyl orange (*7*). Hoffmann (*1*) investigated 19 solutions by determining the solubility of a one to one carbon dioxide–air mixture. A number of the salts used by him give alkaline solutions and several concentrations of some salts were used, so that his conclusion that a 22 per cent sodium chloride solution is best is based on a study of very few practical solutions. Hoffmann further states (*2*) that there is no advantage in using acid in the confining liquid but, on the contrary, its use is likely to cause error, since he found an increase in the solubility of his mixed gas when acid was added to a saturated solution of sodium chloride. Tropsch (*6*) points out that the addition of a little sulfuric acid is of advantage to prevent the liquid from becoming alkaline.

Passauer (*5*) determined the solubility of pure carbon dioxide at 20° C. in 17 different saturated salt solutions. He found that sodium dichromate dissolved the least gas, but it had the disadvantage of being a very viscous solution. Silver nitrate solution was the next best and gave a solution but slightly viscous. Some of these data were checked by other workers (*4*).

Wolf and Krause (*8*) determined the solubility of carbon dioxide in water and in solutions of sodium chloride and calcium chloride. They found that acidulation with sulfuric or hydrochloric acid was useless or harmful, except for alkaline waters. They recommend a nearly saturated sodium chloride solution.

It was believed that an investigation of solubility of carbon dioxide in the usual confining solutions, in solutions of inexpensive salts, and in acid solutions would give data to enable the selection of the most practical confining solution.

Experimental

The apparatus used for this work is shown in Figure 1.

A buret of the mine-air type, *A*, is used, as this gives greater accuracy in the range 75 to 100 ml. Mercury is used as the confining liquid in *A* and in absorption bulb *H*, both being water-jacketed and maintained at 25° C. by a jet of warm air. Buret *A* and pressure compensator *B*, of standard type (*7*), are connected to absorption bulb *H*, which is a 200-cc. balloon flask with a bottom tube attached to a leveling bulb, *K*, containing mercury. Passing through the rubber stopper, *G*, in the neck of bulb *H* are three capillary tubes. The first is from the dropping funnel, *F*, through which the solution is introduced into *H*; the second is the capillary line, *D*, from the buret; and the third is from a small mercury manometer, *E*, by which a known pressure can be maintained above the solution in *H*. The top of the gas bulb is sealed with a cement to prevent leakage around the tubes or rubber stopper *G*. Since the liquids used have little if any effect on rubber, use of rubber is not objectionable. The neck of *H* is clamped into a shaking mechanism which tilts the bulb about 20° each side of vertical, while the bulb is in the constant-temperature bath *I* at all times. The shaker is operated by a motor, reducing gears, and an eccentric (not shown) which turns at 100 r. p. m. The capillary line connecting the buret to the absorption bulb contains a short piece of capillary rubber tubing, *D*, which allows the bulb to be shaken.

The solutions were made up by dissolving the accurately weighed amount of analytical grade salt, calculated as anhydrous salt, into the weighed amount of water, making allowance for any water of crystallization. The per cent salt or acid content is weight per cent, except where volume per cent is noted for acids. The solution was heated to boiling to remove dissolved gases, care being taken to condense and return all water vapor evolved, and the flask was stoppered tightly and cooled to 25° C.

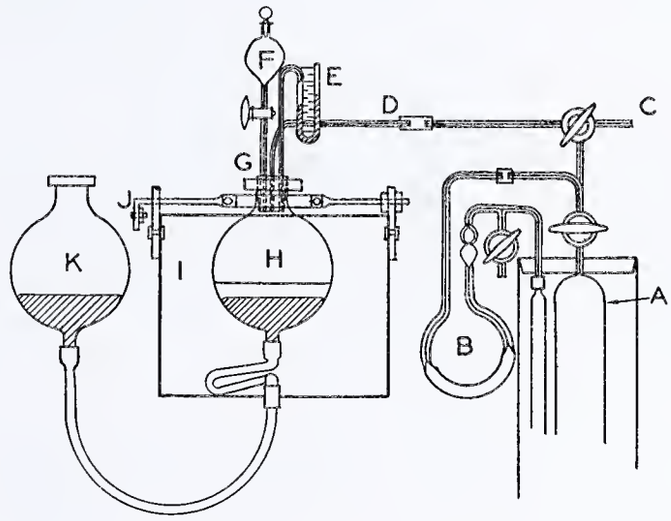

Figure 1. Diagram of Apparatus

Pure carbon dioxide was selected as the gas to be used, as it has the greatest solubility of the gases commonly encountered in ordinary work. It is believed that the data secured in this way have more value than when gaseous mixtures are used. The carbon dioxide was first saturated with water vapor by passing it through a Friedrichs type gas-washing bottle at 25° C. containing solutions being tested.

The gas was introduced to *A* at *C*, 100 ml. of the saturated gas being taken into *A*. Fifty milliliters of the solution were pipetted into bulb *F*, over mercury. By lowering the mercury reservoir, *K*, the solution was drawn into bulb *H*, 0.46 ml. of solution remaining in the stem which connected *F* with *H*. The carbon dioxide in *A* was then introduced into *H* and the latter shaken for 15 minutes. This period of shaking was found to be sufficient to obtain equilibrium between the solution and the carbon dioxide. The pressure in *H* was adjusted by *E* with the barometric pressure, so that the total pressure in *H* was 783.5 mm. Thus, for pure water at 25° C., the partial pressure of the carbon dioxide is 760 mm. Solutions were assumed to have the same vapor pressure as pure water, as the vapor pressure lowering by the salts is negligible for this work. The pressure in *H* during the shaking was adjusted by raising *K* so that the correct reading on *E* was maintained. After the shaking period the carbon dioxide was flushed back to *A* and measured.

Results are shown as milliliters of carbon dioxide at 25° C. and 760 mm. dissolved in 1 ml. of solution at 25° C. The Bunsen absorption coefficient, α, which is the volume of carbon dioxide calculated to 0° C. and 760 mm. dissolved by 1 ml. of solution at 25° C., has also been calculated (*3*). The experimental data and results are shown in Table I.

The data given in Table I are the average of two determinations, accurate to 0.005 in the values of the solubility. The experimental value, $\alpha = 0.754$, for distilled water at 25° C. agrees very well with the International Critical Tables (*3*) value of $\alpha = 0.756$.

Table I. Solubility of Carbon Dioxide in Salt Solution

(Temperature 25° C., total pressure 783.5 mm.)

Salt Used	Concentration	Volume of Solution	Carbon Dioxide Dissolved		Bunsen Coefficient
	Weight %	*Ml.*	*Ml.*	*Ml./ml.[a] soln.*	
None	..	24.54	20.20	0.823	0.754
H_2SO_4	5	24.54	18.30	0.746	0.683
H_2SO_4	10	24.54	17.60	0.717	0.657
NaCl	10	24.54	13.52	0.551	0.505
NaCl	20	49.54	16.54	0.334	0.306
NaCl	20	49.54	16.29	0.328	0.302
H_2SO_4	5				
NaCl	25	49.54	12.75	0.257	0.236
NaCl	20	49.54	17.48	0.352	0.323
HCl	2				
Na_2SO_4	20	49.54	12.9	0.260	0.237
Na_2SO_4	20	49.54	13.07	0.263	0.242
H_2SO_4	5 (vol.)				
Na_3PO_4	10	49.54	13.89	0.280	0.256
H_3PO_4	7				
$CaCl_2$	40	49.54	7.82	0.158	0.144
$MgCl_2$	30	49.54	8.12	0.164	0.150
$ZnCl_2$	50	49.54	19.12	0.386	0.354
$AlCl_3$	25	49.54	12.00	0.243	0.222
$Al_2(SO_4)_3$	20	49.54	10.96	0.221	0.203

[a] Milliliters of CO_2 at 25° C., 760 mm., dissolved per ml. of solution at 25° C.

Discussion of Results

From Table I it is seen that the concentrated solution of calcium chloride dissolves the least carbon dioxide. However, this has three disadvantages as a confining liquid: the solution is quite viscous, it seems to become easily contaminated with impurities and precipitate, and when spilled it does not evaporate and leave crystals but remains as a sticky fluid. The solution may be satisfactory for a confining liquid in gas storage containers, but does not seem suitable for use in the gas analysis apparatus.

The magnesium chloride solution is much less viscous than the calcium chloride solution. The solubility of carbon dioxide is almost equal in the calcium and magnesium chloride solutions, but is much lower than for the sodium chloride or sodium sulfate solutions. Its use in the gas analysis apparatus has the disadvantage that whenever the concentrated hydroxide absorbents come into contact with the magnesium chloride, even though acidified, a precipitate of magnesium hydroxide is formed, which plugs up the capillary tube. The use of magnesium chloride is recommended when this contact with alkalies is not possible.

The solubilities in 20 per cent sodium sulfate and 25 per cent sodium chloride are nearly equal; however, the 25 per cent sodium chloride is more nearly saturated than the 20 per cent sodium sulfate, so the latter is recommended. The addition of 5 per cent by weight of sulfuric acid to 20 per cent sodium chloride and 5 per cent by volume of sulfuric acid to 20 per cent sodium sulfate has been shown to produce a negligible change in the solubility of carbon dioxide in these solutions. As a confining solution must never be alkaline, the addition of acid is necessary, and no error is introduced as suggested by Hoffmann (*2*).

Conclusions

A 20 per cent by weight sodium sulfate and 5 per cent by volume sulfuric acid solution is recommended as the most practical confining liquid for use in technical gas analysis equipment.

The addition of acid to sodium sulfate or sodium chloride solutions causes no appreciable increase in the solubility of carbon dioxide, and is necessary to prevent the solution from becoming alkaline at any time.

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Determination of Chloride

A Modification of the Volhard Method

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The Volhard method for the determination of chloride has been subjected to many modifications. Kolthoff (*3*) in a review of the subject points out the fundamental errors in several of the proposed methods and concludes that only one, the method of Schoorl (*5*), gives accurate results. This procedure is somewhat tedious, and since it requires special precautions it is limited in application. The method in general use at the present time requires the removal of the precipitated silver chloride by filtration before back-titrating with potassium thiocyanate. A modification is desirable which eliminates this filtration. Recently Stschigol (*6*) has proposed covering the chloride solution with a layer of toluene or benzene. These immiscible liquids cause the silver chloride to be drawn to the interface and thus remove it from the aqueous solution. This principle was suggested earlier by Rothmund and Burgstaller (*4*), but the method has certain disadvantages as shown by Kolthoff (*3*). Furthermore, the authors have observed that the end point is partially obscured because the precipitated silver chloride turns dark more rapidly in the presence of these organic liquids.

The principal objection to the Volhard method is the fading end point when the silver chloride is not removed, due to the fact that silver chloride is more soluble than silver thiocyanate. Kolthoff (*3*) suggests the subtraction of 0.7 per cent of the percentage of chloride found in order to correct for adsorption of silver nitrate on the silver chloride and on the silver thiocyanate. In this paper a modification is proposed which reduces the errors mentioned above to negligible values and considerably shortens the time required for a determination. Repeated trials in the hands of several operators have given accurate results with errors no greater than the probable errors in reading the volumetric apparatus.

In view of the successful use by Caldwell of the addition of an organic substance to improve the end point in the iodometric determination of copper (*1*), this principle was applied to the Volhard titration. It was found that nitrobenzene had the desired properties. The experimental evidence seems to indicate that in the presence of nitrobenzene no appreciable amount of silver nitrate is carried down and that the nitrobenzene forms an insoluble layer over the precipitate, so that the rate of solution of the silver chloride is reduced to such an extent that it does not interfere in the thiocyanate titration.

Experimental

Silver Nitrate. A 0.1 *N* solution of silver nitrate was prepared by dissolving the appropriate weight of reagent silver

nitrate which had been recrystallized twice and dried at 70° C. in a vacuum desiccator over sulfuric acid.

Potassium Thiocyanate. An approximately 0.05 *N* solution was prepared and standardized against the silver nitrate solution.

Sodium Chloride. This was prepared by precipitating a sample of reagent quality sodium chloride three times from aqueous solution with concentrated hydrochloric acid. It was dried at dull redness for 30 minutes.

Nitrobenzene. A reagent grade gave no precipitate with alcoholic silver nitrate and was used without further purification.

Ferric Alum Indicator. Concentrated, freshly boiled nitric acid was added to a saturated solution of ferric alum until the solution became greenish yellow.

Procedure

Titrations were made in 250-ml. glass-stoppered bottles. A solution (25 to 50 ml.) containing from 0.0483 to 0.2606 gram of sodium chloride, free from the usual interfering ions, was acidified with 8 to 10 drops of concentrated nitric acid and 1 ml. of nitrobenzene was added for each 0.05 gram of chloride. Standard silver nitrate was added until an excess of 1 to 4 ml. of 0.1 *N* solution was present. The bottle was then tightly stoppered and shaken vigorously until the silver chloride settled out in large spongy flakes. Usually 30 to 40 seconds' agitation was required. It was found that a perfectly clear supernatant solution was not necessary. Fine droplets of nitrobenzene were often left in suspension. However, nearly all the nitrobenzene seemed so closely attached to the silver chloride that there was little evidence of it as a separate phase.

One milliliter of ferric alum indicator was added and the titration completed with standard thiocyanate solution. The ferric alum acted as an effective flocculating agent and coagulated any suspended matter which was present. Standard potassium thiocyanate solution was added slowly with gentle swirling until a pink color was produced. Usually a false end point appeared one drop before the true end point; it faded in about 30 seconds and may have been due to the desorption of the last traces of silver nitrate from the precipitate. The next drop of thiocyanate produced a decided color change which persisted 10 to 15 minutes. Titrations should be made at temperatures below 25° C., as is customary in other titrations with thiocyanate.

Samples of pure sodium chloride were dissolved and titrations were made according to the method just described. The results are shown in Table I.

Table I. Results of Test Analyses

Sodium Chloride Taken	Sodium Chloride Found	Difference
Gram	*Gram*	*Gram*
0.0483	0.0484	+0.0001
0.0486	0.0487	+0.0001
0.0491	0.0489	−0.0002
0.0492	0.0491	−0.0001
0.1005	0.1003	−0.0002
0.1011	0.1013	+0.0002
0.1011	0.1010	−0.0001
0.1132	0.1132	0.0000
0.1210	0.1209	−0.0001
0.2006	0.2004	−0.0002
0.2211	0.2207	−0.0004
0.2508	0.2506	−0.0002
0.2518	0.2520	+0.0002
0.2605	0.2605	0.0000
0.2606	0.2607	+0.0001

The method was checked by another operator who used a standard silver nitrate solution prepared with specially purified silver supplied by C. W. Foulk. The silver was prepared by Foulk and Pappenhagen (*2*) in a study of silver as an ultimate standard in acidimetry. It was dissolved in nitric acid and the solution diluted to a definite volume, so that the final strength was approximately 0.1 *N*. Several titrations were made with this solution with results equally as good as those shown in Table I.

Discussion

Nitrobenzene, as used in this determination, exhibits the interesting property of inhibiting the darkening of silver chloride in light and this also improves the end point. In several other respects it is superior to other proposed organic liquids. A very small volume is required, and since it is heavier than water it does not form a troublesome layer over the aqueous solution. Most of it attaches itself to the silver chloride, so that its presence is hardly noticed in the subsequent thiocyanate titration.

Divalent ions, such as calcium and barium, have no apparent effect on the functioning of the nitrobenzene. The method was used with success by O. C. Dermer in this laboratory for the titration of solutions containing piperidine hydrochloride.

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Determination of Perchlorates

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Mellor states (*2*) that "Williams (*4*) found that the perchlorates are reduced by titanium trichloride, while the chlorates are not affected, and based a process for the volumetric determination of perchlorates—in the presence of chlorates and chlorides—on this reaction." However, he also states (*3*) that "chlorates and perchlorates are reduced to chlorides" by titanium trichloride. Knecht and Hibbert (*1*) give directions for the determination of both chlorates and perchlorates with titanous chloride. The chlorates are quantitatively reduced in the cold while the perchlorates are not appreciably reduced in dilute aqueous solution, even on prolonged boiling. The perchlorates are completely reduced, however, by a strong solution of titanous chloride in a fairly strong sulfuric acid solution.

The two statements of Mellor and that of Knecht and Hibbert do not agree, and a closer investigation of the work of Williams shows that he boiled weighed quantities of potassium chlorate and ammonium perchlorate with an excess of titanous chloride in the presence of sulfuric acid and then titrated the excess of titanous chloride with ferric alum. This should reduce both the perchlorate and chlorate and he states in his results that "the table below gives results (for perchlorate) after the chlorate had been allowed for." He, therefore, undoubtedly did not find that the chlorates were unaffected by titanous chloride, as stated by Mellor, but corrected his results for the known amount of chlorate present.

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Indicator Properties of Dinitroaniline Azo Dyestuffs

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In a previous article (*1*) the author described a new indicator, 2,4-dinitroaniline-azo-1-naphthol-3,6-disulfonic acid, which he called nitrazine yellow. Since then many similar dyes have been investigated, using 2,4- and 2,6-dinitroaniline and their sulfonic acids as diazotable amines and 1- and 2-naphthol and their sulfonic acids as azo components. All couplings were made in dilute sulfuric acid solution. The results are shown in Table I.

Comparison of these dyes indicates:

1. Only azo components with para coupling—1-naphthol, and 1,6-, 1,7-, and 1,8-naphtholsulfonic acids—give indicators of strong color contrast and relatively narrow pH range.
2. The 2,4- position of the nitro groups of the diazo components is preferable to the 2,6-position, as the former gives bluer and brighter, the latter redder and duller shades in alkaline solution and therefore less color contrast.
3. A few of the new dyes compare with nitrazine yellow in color intensity and contrast, but are inferior in solubility and narrowness of pH range.

Other dyes prepared in this connection are:

2,4-Dinitroaniline → H acid; color range red to blue, pH range 8.0 to > 10.

2,4-Dinitroaniline → benzoyl H acid; color range red to blue, pH range 5.8 to 7.6.

2,4-Dinitro-1-naphthylamine-7-sulfonic acid → 1-naphthol-6-sulfonic acid; color range dull orange to greenish blue, pH range 5.6 to 7.4.

Obviously no improvements can be expected by modifying the indicator molecule along lines as indicated by these three dyes.

In preparing nitrazine yellow a red dye is always formed simultaneously, and can be separated from the indicator proper by repeated fractionated salting out, nitrazine yellow being precipitated first. Probably this red dye, which also turns blue in alkaline solution (pH range 9.6 to >10) is the ortho azo dye, while nitrazine yellow is the para isomer. Because of the difficulty of completely reducing azo dyes which contain a nitro group in ortho position to the azo group—formation of triazoles—no experimental proof for this supposed isomerism can be brought so far.

Concerning the nature of the intermolecular rearrangement which these dyestuffs undergo in acid and alkaline solution, respectively, it has been proved that the blue form of nitra-

Table I. Indicator Properties

	2,4-Dinitroaniline	2,6-Dinitroaniline	2,4-Dinitroaniline-6-sulfonic Acid	2,6-Dinitroaniline-4-sulfonic Acid
		1-naphthol		
Dry	Red-brown	Orange	Red-brown	Yellow
Sulfuric acid	Blue	Violet	Purple	Bright purple
Water	Insoluble	Insoluble	Slightly soluble	Slightly soluble
Alcohol	Slightly soluble	Slightly soluble	Very soluble	Insoluble
Acid	Insoluble	Yellow	Bright yellow	Pale yellow
Alkali	Blue	Violet	Bright blue	Blue
pH	7.8 to 9.6 in alcoho	4.4 to 7.4 in alcohol	5.2 to 8.2	6.2 to 7.3
		1-naphthol-4-sulfonic acid		
Dry	Dark red	Red	Dark red	Red
Sulfuric acid	Blue	Red	Dull red-brown	Dull red
Water	Slightly soluble	Slightly soluble	Soluble	Soluble
Alcohol	Soluble	Soluble	Soluble	Soluble
Acid	Orange	Orange	Yellow	Dull yellow
Alkali	Blue	Blue-red	Dull green	Dull wine red
pH	8 to >10	>10	5.8 to 7.8	6.4 to 8.0
		1-naphthol-5-sulfonic acid		
Dry	Red-brown	Could not be isolated	Brown	Red-brown
Sulfuric acid	Dull brown		Dull brown	Dull brown
Water	Slightly soluble		Soluble	Soluble
Alcohol	Soluble		Soluble	Slightly soluble
Acid	Dull orange		Dull orange	Dull orange
Alkali	Blue		Blue	Violet
pH	7.0 to 10.4		6.6 to 9.0	6.0 to 8.8
		1-naphthol-6-sulfonic acid		
Dry	Red	Red	Bright yellow	Orange
Sulfuric acid	Purple	Bright purple	Bright purple	Bright purple
Water	Soluble	Soluble	Soluble	Soluble
Alcohol	Insoluble	Insoluble	Soluble	Insoluble
Acid	Yellow	Dull orange	Bright yellow	Bright yellow
Alkali	Bright blue	Wine red	Bright blue	Violet
pH	6.6 to 8.6	5.4 to 7.0	3.8 to 7.4	5.0 to 7.2
		1-naphthol-7-sulfonic acid		
Dry	Brown	Dark brown	Could not be isolated	Brown
Sulfuric acid	Purple	Bright purple		Bright purple
Water	Slightly soluble	Soluble		Soluble
Alcohol	Slightly soluble	Very soluble		Slightly soluble
Acid	Yellow	Yellow		Dull orange
Alkali	Blue	Purple		Blue-red
pH	6.6 to 8.6	5.0 to 7.4		3.0 to 5.8
		1-naphthol-8-sulfonic acid		
Dry	Yellow	Yellow	Yellow	Dull red
Sulfuric acid	Purple	Bright purple	Bright purple	Bright purple
Water	Slightly soluble	Soluble	Very soluble	Very soluble
Alcohol	Slightly soluble	Soluble	Soluble	Insoluble
Acid	Bright yellow	Bright yellow	Yellow	Yellow
Alkali	Bright blue	Blue, slightly red	Blue, slightly green	Blue
pH	7.6 to 10	6.8 to 8.8	5.8 to 8.4	6.4 to 8.2
		1-naphthol-3,6-disulfonic acid		
Dry	Red	Red	Could not be isolated	Red
Sulfuric acid	Bright blue	Bright purple		Bright purple
Water	Soluble	Very soluble		Very soluble
Alcohol	Insoluble	Insoluble		Insoluble
Acid	Bright yellow	Yellow		Bright yellow
Alkali	Bright blue	Purple		Dull violet
pH	6.0 to 7.0	5.4 to 7.4		5.2 to 8.0

Table I. (*Continued*)

	2,4-Dinitroaniline	2,6-Dinitroaniline	2,4-Dinitroaniline-6-sulfonic Acid	2,6-Dinitroaniline-4-sulfonic Acid
		2-naphthol		
Dry	Bright orange	Bright red	Bright red	Bright orange
Sulfuric acid	Violet	Red	Violet	Blue-red
Water	Insoluble	Insoluble	Very slightly soluble	Soluble
Alcohol	Very slightly soluble	Insoluble	Insoluble	Insoluble
Acid	Yellow in alcohol	.....	Orange	Orange
Alkali	Blue in alcohol	.....	Blue	Blue
pH	>10	.....	8.8 to >10	8.4 to <10
		R salt		
Dry	Bright red	Bright red	Orange	Orange
Sulfuric acid	Bright purple	Bright red	Orange	Orange
Water	Very soluble	Soluble	Very soluble	Very soluble
Alcohol	Insoluble	Insoluble	Insoluble	Insoluble
Acid	Red	Orange	Yellow	Orange
Alkali	Dull violet	Red	Green	Wine red
pH	>10	8.8 to >10	7.8 to 9.8	8.2 to 9.8
		G salt		
Dry	Bright red	Could not be isolated	Could not be isolated	Could not be isolated
Sulfuric acid	Orange			
Water	Very soluble			
Alcohol	Insoluble			
Acid	Orange			
Alkali	Dull violet			
pH	>10			

zine yellow contains three sodium atoms. This salt can be isolated by precipitating the indicator from a strongly alkaline solution with alcohol; it forms a dark powder of metallic luster, is quite stable, can be dried at 100° C., and has been analyzed.

While in the dyes derived from 2,6-dinitroaniline it must be an ortho nitro group which becomes ionogen in alkaline solution, it is an open question which of the two nitro groups assumes this function in the indicators derived from 2,4-dinitroaniline.

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Baumé-Purity-Moisture Tables for Corn Sirup

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The moisture content of a corn sirup or corn sugar for a given Baumé has been found dependent upon the purity of the sirup involved. Increasing purity results in increasing dry substance for a given Baumé.

The dry substance values for corn sirup, as found in several tables in use among the trade, have been found too high. A new table employing purity as well as Baumé has been constructed for the entire range of the usual starch hydrolytic products.

Several corn sirups and corn sugars from different refineries have been analyzed for dry substance, with results which indicate that for equal Baumé and purity the moisture content is the same.

Over one billion pounds of corn sirup are refined annually in the United States. Corn sirup is produced from starch by acid hydrolysis in three purities—low, regular, and high—and consists of dextrin, maltose, and dextrose. Purity is defined within the industry as the amount of reducing sugars expressed as dextrose on a dry substance basis. As the actual dry substance in corn sirup is difficult to determine, the custom in the industry has been to express the purity on a Brix solids basis as a matter of convenience, even though the Brix solids are not the actual solids.

The term "purity" is necessary, as the same sirup is sold at different gravities. In selling, gravity is used as a measure of the dry substance contained in the sirup, and will run from 41° to 47° Bé., being expressed at 100° F. Sirups with a gravity of 41° and 42° are more often termed "mixing sirups" and are largely used by manufacturers of mixed table sirups. Confectioners' sirup runs from 43° to 46° Bé., the bulk being sold at 43° Bé., as this gravity represents the practical limit at which this heavy viscous sirup may be handled economically. In recent years considerable 42° Bé. sirup has been sold to confectioners, as it is handled more easily in the piping systems which have been installed in candy factories. The purities produced by each refiner vary to a small degree, but the range and major use of the three types produced are:

Low purity	30 to 35	Brewery use as "body sirups"
Regular purity	40 to 45	Confectionery trade
High purity	50 to 55	Brewery and bakery trade

The bulk of the sirup sold is of regular or medium purity.

In the mechanical separation of starch from corn, a yield of 30 to 33 pounds per bushel is obtained. In the subsequent hydrolysis of starch, there is a chemical gain, the amount depending upon whether sirup or sugar is produced. Thus, the yield in dry substance of the various products produced on the basis of the dry substance corn used became an important measure of the efficiency of a refinery. It was soon found that the Brix solids could not be used for the measure of dry substance in corn sirup and sugar, so special tables were constructed for the usual range of sirups produced, retaining the Brix solids for the basis of the purity determination. Each refinery either constructed a special Baumé-moisture table or adopted one already in use at another refinery. Once a table was in use, corrections became impossible, as the management decreed that such a change would render comparison with past factory performance impossible. If each factory was self-contained, this attitude might have been justified, but in selling sirups on the market, these various moisture tables were given customers, who at once noticed that one table gave more dry substance for a given

Baumé than another. The manufacturer whose table showed high moisture values soon realized that he was at a sales disadvantage which was hard to explain, and took the easiest way out by adopting the table of the largest producer.

The confusion to the customer was further enhanced by the use of the Old Dutch scale hydrometer of 144 modulus in the corn products industry. Thus, a salesman would quote data based on a 144 modulus spindle, which the customer would use with his hydrometer based on the Bureau of Standards modulus of 145. The relationship between the two hydrometers is shown in Table I, which also includes the moisture values in use by the largest producer in the industry, column I, and those in use by another refiner, column II.

Table I. Hydrometer Relationship

M-144	M-145	Moisture I	Moisture II
		%	%
38.73	39.00	26.0	26.0
39.00	39.27	25.5	25.5
39.73	40.00	24.0	24.0
40.00	40.27	23.5	23.5
40.71	41.00	22.1	22.1
41.00	41.29	21.5	21.5
41.71	42.00	20.9	20.9
42.00	42.29	19.5	19.5
42.71	43.00	18.2	18.1
43.00	43.29	17.7	17.5
43.69	44.00	16.6	16.1
44.00	44.31	16.1	15.5
44.69	45.00	15.0	14.1
45.00	45.31	14.5	13.5
45.68	46.00	....	12.1
46.00	46.32	....	11.4

The errors in this table soon became apparent to the users of corn sirup. Candy makers claimed that from their yield figures the moisture of corn sirup was nearer 20 per cent than the 18.2 per cent of the table, making no allowance for 0.1° to 0.2° Bé. overage which is always given. Gum makers, who use 45° Bé. sirup, claimed that this sirup had over 15 per cent moisture by their yield figures.

This confusion among the trade, and the discrepancy between various refiners who use their own tables, have prompted the work recorded in this paper. The authors have made a very careful study of the Baumé-moisture-purity values for sirups of their own manufacture and those of competitors. The table (Table II) as originally constructed was for Baumé-moisture only, but it was found during the investigation that the moisture content decreased for a given Baumé as the purity increased. Thus, in place of the limited corn sirup moistures originally planned, the work has been increased to cover the entire range of starch hydrolytic products.

Methods of Analysis

Moisture. The moisture values given in Table II were made according to the A. O. A. C. method of drying on sand (*1*). Difficulties are encountered with this method on products containing dextrin, as it is almost impossible to remove the last traces of moisture. To overcome this difficulty, the present authors introduced the toluene distillation method with certain modifications for corn sirup (*2*) and this procedure has been used in the following work. However, it was difficult to be sure of the removal of the last trace of moisture from high gravity sirup, and it was necessary to adopt an increasing distillation time as the gravity increased, to secure accurate results. The schedule used was: 39° Bé. for 6 hours' distillation time, with an increase of one hour for each degree increase in gravity. Thus, 47° Bé. required 14 hours' distillation time.

Baumé. The Baumé was obtained according to the usual commercial practice. The sirup in a glass cylinder was placed in a water bath at 140° ± 5° F., and when free from air the hydrometer was introduced. Several hydrometer readings with corresponding temperature observations were made. The data were corrected to 100° F., employing the correction of 4° F. = 0.1° Bé., and averaged. The hydrometer used was based on a modulus of 145, standardized at 60° F., with a Bureau of Standards certificate. This hydrometer was checked at intervals, at room temperature, against a similar hydrometer with a Bureau of Standards certificate. The thermometer used was a precision instrument.

Table II. Baumé-Moisture-Purity Results

No.	Baumé Corrected to 100° F.	Moisture		Purity Actual solids	Purity Brix solids	Purity $\frac{\text{Purity BS}}{\text{Purity AS}} \times 100$
1	39.16	27.76	27.78	36.5	34.7	95.3
	42.19	21.70	21.75	36.5	34.8	
	42.57	20.94	20.95	36.4	34.8	
	44.22	17.64	17.66	..	..	
2	39.32	27.34	27.39	37.8	35.8	95.2
	41.17	23.64	23.68	37.8	35.9	
	42.44	21.08	21.12	37.9	36.0	
	42.67	20.62	20.64	..	36.0	
	44.79	16.41	16.44	..	36.0	
	45.04	15.90	15.97	..	..	
	47.14	11.71	11.77	..	..	
3	38.95	28.02	28.08	39.3	37.4	95.2
	41.02	23.90	23.90	39.4	37.5	
	43.11	19.61	19.65	39.5	37.6	
	45.46	14.95	14.98	..	37.5	
4	38.97	27.82	27.88	41.9	40.1	95.8
	41.12	23.53	23.21	41.8	40.1	
	41.29	23.18	19.08	41.8	40.2	
	43.35	19.05	14.47	41.9	..	
	45.64	14.45	...	..	..	
5	39.84	26.01	26.05	43.2	41.3	95.4
	41.47	22.71	22.73	43.3	41.3	
	46.16	13.28	13.31	43.3	41.4	
6	39.19	27.34	27.38	43.3	41.6	96.1
	41.47	22.74	22.75	43.4	41.7	
	43.65	18.33	18.37	43.5	41.7	
	45.72	14.19	14.20	43.5	..	
7	38.97	27.64	27.66	45.3	43.3	95.8
	40.80	23.95	23.99	45.3	43.4	
	42.82	19.87	19.91	45.4	43.4	
	44.83	15.82	15.86	..	..	
	46.02	13.41	13.49	..	..	
8	38.63	27.70	27.78	54.6	52.7	96.5
	41.20	22.51	22.55	54.7	52.8	
	42.38	20.14	20.15	54.8	52.9	
	45.26	14.29	14.32	..	..	
	46.95	10.95	11.02	..	..	
9	39.33	25.71	25.77	65.4	63.8	97.5
	41.01	22.29	22.31	65.4	63.8	
	42.96	18.31	18.31	65.5	..	
	45.17	13.80	13.83	..	..	
10	39.06	25.94	25.96	69.8	68.3	97.7
	39.17	25.67	25.73	69.9	68.4	
	41.41	21.11	21.15	70.1	68.4	
	43.42	16.99	17.00	..	..	
	44.80	14.16	14.19	..	..	
11	38.65	26.28	26.32	78.7	77.6	98.6
	39.65	24.13	24.19	78.7	77.6	
	41.63	20.15	20.18	78.8		
	43.09	17.13	17.17	..	..	
	45.68	11.83	11.88	..	..	
12	39.26	24.89	24.90	81.9	80.6	98.6
	40.13	23.04	23.05	82.0	80.7	
	41.36	20.54	20.54	82.1	80.8	
	43.21	16.69	16.73	..	..	
	44.92	13.16	13.19	..	..	
13	39.45	24.14	24.19	86.6	85.6	99.0
	40.89	21.19	21.21	86.7	85.8	
	43.70	15.34	15.36	86.8	85.9	
	45.93	10.75	10.75	..	..	
14	39.05	24.93	24.95	88.1	87.3	99.0
	41.06	20.73	20.79	88.2	87.3	
	43.21	16.31	16.35	88.2	87.4	
	45.72	11.11	11.13	..	..	
15	39.56	23.76	23.79	89.7	88.9	99.2
	41.03	20.71	20.74	89.7	89.0	
	43.24	16.10	16.14	89.8	89.0	
	45.02	12.43	12.43	..	..	

Nos. 7, 8, 12, 13, and 15, Union Starch & Refining Co., factory production.
Nos. 2, 3, 9, 10, 11, Union Starch & Refining Co., laboratory products; factory conditions.
Nos. 1 and 14, manufactured by A. E. Staley Mfg. Co.
No. 4, manufactured by Penick & Ford, Ltd.
No. 5, manufactured by The Clinton Company.
No. 6, manufactured by Corn Products Refining Company.

The present authors believe that some of the confusion on Baumé-moisture determinations is caused by inaccurate gravity determinations. The error is introduced by the failure to remove all traces of air from the sirup. This is particularly true of routine determinations of gravities on factory shipments, which are usually required in a hurry. Common practice is to make all shipments 0.1° Bé. heavy,

but sirup has been procured on the open market which spindled as high as 0.7° Bé. heavy. Samples which run 0.3 to 0.4° Bé. heavy are fairly common.

Purity. The purity of corn sirup or sugar is controlled in the refinery by testing the liquor from the neutralizer, immediately after the conversion. The usual procedure is to obtain the Brix of the liquor and make a suitable dilution, after which the reducing sugars are determined as dextrose. The latter figure is then expressed on a Brix solids basis. Sugar liquor will run from 28 to 32 Brix, and sirup from 34 to 38 Brix. The procedure on the analysis of a finished sirup or sugar is to reduce it to the same Brix range, and employ the same method of analysis.

For convenience, purity has been expressed in Table II on actual solids and on Brix solids. The titration method of Lane and Eynon (*3*), employing methylene blue as an indicator, was used for each method. The procedure for actual solids has already been described (*2*). For the Brix solids purity, a given quantity of sirup or sugar was diluted to fall within 30 to 36 Brix, on a precision instrument standardized at 20° C. (68° F.). Twenty-five milliliters were taken, and diluted to 500 ml., from which point the procedure was the same as for actual solids. As the purity increased, the amount of sample used was decreased, so as to maintain a 12- to 15-ml. titration volume for 25 ml. of Fehling's solution.

The actual solids purities in Table II are the average of duplicate titrations made on sirup of different densities, thus employing a different dry substance value in each case. The Brix solids purities are the average of duplicate titrations on different dilutions of the sirup to the Brix range indicated above.

These data were plotted on millimeter graph paper of such size that 0.02 per cent moisture and 0.02° Bé. equaled 1 mm. A straight line fitted the plotted points with each purity. From this graph, purity-moisture values were obtained for the even Baumé's and are given in Table III.

Table III. Purity-Baumé-Moisture

Purity, Actual Solids	39.0°	40.0°	41.0°	42.0°	43.0°	44.0°	45.0°	46.0°	47.0°
36.5	28.09	26.09	24.09	22.09	20.10	18.10	16.10	14.11	12.11
37.8	28.00	26.00	24.01	22.01	20.01	18.02	16.03	14.03	12.04
39.3	27.94	25.93	23.92	21.91	19.91	17.90	15.89	13.88	11.87
43.2	27.69	25.68	23.67	21.66	19.65	17.65	15.64	13.63	11.63
45.3	27.56	25.55	23.54	21.54	19.53	17.53	15.53	13.53	11.53
54.7	26.98	24.96	22.94	20.92	18.90	16.89	14.87	12.85	10.83
65.4	26.39	24.35	22.31	20.27	18.23	16.19	14.15	12.11	...
70.0	26.07	24.02	21.97	19.92	17.89	15.84	13.80	11.76	...
78.7	25.59	23.53	21.47	19.41	17.35	15.30	13.25	11.20	...
82.0	25.38	23.32	21.26	19.20	17.14	15.08	13.02	10.96	...
86.8	25.13	23.05	20.97	18.89	16.81	14.74	12.67	10.60	...
88.2	25.05	22.98	20.91	18.83	16.76	14.68	12.61	10.54	...
89.7	24.96	22.88	20.80	18.72	16.64	14.56	12.48	10.40	...

Table IV. Purity-Baumé-Moisture

Purity, Actual Solids	39.0°	40.0°	41.0°	42.0°	43.0°	44.0°	45.0°	46.0°	47.0°
35	28.18	26.18	24.18	22.18	20.19	18.20	16.19	14.21	12.21
40	27.88	25.88	23.87	21.87	19.87	17.87	15.86	13.86	11.86
50	27.29	25.27	23.25	21.24	19.22	17.20	15.18	13.17	11.15
60	26.70	24.67	22.64	20.61	18.57	16.54	14.51	12.47	10.44
70	26.12	24.07	22.02	19.97	17.92	15.87	13.82	11.77	...
80	25.53	23.47	21.40	19.34	17.27	15.21	13.14	11.08	...
90	24.94	22.86	20.78	18.70	16.62	14.54	12.46	10.38	...

These data were plotted on the same size of graph paper, with purity and moisture as abscissas. A straight line was found to fit the points for each Baumé. From this graph, Table IV has been prepared, giving moisture values for even purity-Baumé values.

The ratio $\frac{\text{Brix solids purity}}{\text{actual solids purity}} \times 100$ was plotted and a straight line was found to fit the points. From this graph Table V has been prepared to show this relationship.

Table V

Purity, Actual Solids	$\frac{\text{Brix Solids Purity}}{\text{Actual Solids Purity}} \times 100$
	%
35	95.0
40	95.4
50	96.2
60	96.9
70	97.7
80	98.4
90	99.2

For the convenience of the chemists in the confectionery, bakery, brewing, and rayon industries, and as a means of standardizing a table within the corn products industry itself the authors present Table VI.

Table VI. Purity-Baumé-Moisture, Corn Sirup and Corn Sugar

(Table at 100° F.; hydrometer, 145 M, 60° F.)

Purity AS	Purity BS	Baumé 39°	40°	41°	42°	43°	44°	45°	46°	47°
40	38.2	27.9	25.9	23.9	21.9	19.9	17.9	15.9	13.9	11.9
41	39.1	27.8	25.8	23.8	21.8	19.8	17.8	15.8	13.8	11.8
42	40.1	27.8	25.8	23.8	21.7	19.7	17.7	15.7	13.7	11.7
43	41.1	27.7	25.7	23.7	21.7	19.7	17.7	15.7	13.7	11.7
44	42.1	27.6	25.6	23.6	21.6	19.6	17.6	15.6	13.6	11.6
45	43.1	27.6	25.6	23.6	21.6	19.5	17.5	15.5	13.5	11.5
46	44.1	27.5	25.5	23.5	21.5	19.5	17.5	15.5	13.4	11.4
47	45.1	27.5	25.5	23.4	21.4	19.4	17.4	15.4	13.4	11.4
48	46.1	27.4	25.4	23.4	21.4	19.4	17.3	15.3	13.3	11.3
49	47.1	27.4	25.3	23.3	21.3	19.3	17.3	15.3	13.2	11.2
50	48.1	27.3	25.3	23.3	21.2	19.2	17.2	15.2	13.2	11.2
51	49.1	27.2	25.2	23.2	21.2	19.2	17.1	15.1	13.1	11.1
52	50.1	27.2	25.2	23.1	21.1	19.1	17.1	15.1	13.0	11.0
53	51.1	27.1	25.1	23.1	21.1	19.0	17.0	15.0	13.0	10.9
54	52.1	27.1	25.0	23.0	21.0	19.0	16.9	14.9	12.9	10.9
55	53.1	27.0	25.0	22.9	20.9	18.9	16.9	14.8	12.8	10.8
56	54.1	26.9	24.9	22.9	20.9	18.8	16.8	14.8	12.8	10.7
57	55.1	26.9	24.9	22.8	20.8	18.8	16.7	14.7	12.7	10.7
58	56.1	26.8	24.8	22.8	20.7	18.7	16.7	14.6	12.6	10.6
59	57.1	26.8	24.7	22.7	20.7	18.6	16.6	14.6	12.5	10.5
60	58.1	26.7	24.7	22.6	20.6	18.6	16.5	14.5	12.5	10.4
65	63.3	26.4	24.4	22.3	20.3	18.2	16.2	14.2	12.1	..
70	68.4	26.1	24.1	22.0	20.0	17.9	15.9	13.8	11.8	..
75	73.5	25.8	23.8	21.7	19.7	17.6	15.5	13.5	11.4	..
80	78.7	25.5	23.5	21.4	19.3	17.3	15.2	13.1	11.1	..
81	79.7	25.5	23.4	21.3	19.3	17.2	15.1	13.1	11.0	..
82	80.8	25.4	23.3	21.3	19.2	17.1	15.1	13.0	10.9	..
83	81.9	25.4	23.3	21.2	19.2	17.1	15.0	12.9	10.9	..
84	83.0	25.3	23.2	21.2	19.1	17.0	14.9	12.9	10.8	..
85	84.0	25.2	23.2	21.1	19.0	16.9	14.9	12.8	10.7	..
86	85.1	25.2	23.1	21.0	19.0	16.9	14.8	12.7	10.7	..
87	86.1	25.1	23.0	21.0	18.9	16.8	14.7	12.7	10.6	..
88	87.2	25.1	23.0	20.9	18.8	16.8	14.7	12.6	10.5	..
89	88.2	25.0	22.9	20.8	18.8	16.7	14.6	12.5	10.4	..
90	89.3	24.9	22.9	20.8	18.7	16.6	14.5	12.5	10.4	..
91	90.4	24.9	22.8	20.7	18.6	16.6	14.5	12.4	10.3	..
92	91.4	24.8	22.7	20.6	18.6	16.5	14.4	12.3	10.2	..
Lb. per gal.		11.33	11.43	11.54	11.66	11.77	11.89	12.01	12.13	12.25

Water, 8.279

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Carbon Paper and Typewriter Ribbons. The National Bureau of Standards has prepared Letter Circular 424, in which it is shown how anybody can make writing tests of carbon paper and typewriter ribbons, and select for himself the kinds that are best adapted to his special needs. Brief accounts are also given of the manufacture of these materials, and it is pointed out how their physical properties and composition are related to their writing qualities.

A serviceability or wear-down test and a manifolding test for carbon paper are described, as well as a wear-down test for typewriter ribbons, and a method for testing ribbons for the clogging of type.

Determination of Available Chlorine in Hypochlorite Solutions by Direct Titration with Sodium Thiosulfate

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THE use of sodium thiosulfate for the direct volumetric determination of available chlorine in a hypochlorite solution has been considered unsatisfactory and the literature is confusing as to the exact reaction which takes place. In many discussions of the subject, the author avoids the reaction of chlorine by giving the iodine reaction and leaves the impression that chlorine acts in the same manner as iodine and according to the following well-known equation:

$$2Na_2S_2O_3 + Cl_2 \longrightarrow Na_2S_4O_6 + 2NaCl \qquad (1)$$

Mohr (*4*) states that eight equivalents of chlorine from chlorine water are consumed in the complete oxidation of one mole of sodium thiosulfate, but infers that constant results cannot be obtained when this method is used for determining available chlorine. Lunge (*3*) gives the theoretical reaction for chlorine on sodium thiosulfate as follows:

$$Na_2S_2O_3 + 8Cl + 5H_2O \longrightarrow H_2SO_4 + Na_2SO_4 + 8HCl \qquad (2)$$

He states that this reaction does not go to completion in the manner indicated, and that in all cases the amount of thiosulfate consumed is greater than is required by Equation 2 and less than is required by Equation 1. He suggests the possibility of two or more reactions taking place to form different oxidation products of sulfur, and states that sulfur, sulfur dioxide, and hydrogen sulfide were all observed during different conditions of the experiment. Diénert and Wandenbulcke (*2*), when attempting to formulate a method for calculating the amount of sodium thiosulfate solution required to neutralize the chlorine in chlorine water, obtained results which were erratic and which were influenced by the alkali and carbonate content of the solution. Bloxam (*1*) gives Reaction 2 without discussion. Treadwell and Hall (*6*) state that chlorine and bromine react like iodine on sodium thiosulfate when they are not present in excess, but that when they are present in excess the tetrathionate is oxidized to the sulfate and sulfuric acid with the deposition of sulfur which in turn is gradually oxidized to sulfate.

In an attempt made in this laboratory to make use of either Reaction 1 or 2 in the volumetric estimation of available chlorine in a hypochlorite solution, using starch–potassium iodide paper as an outside indicator, the results obtained were erratic and the amount of thiosulfate consumed was not correct for the satisfaction of either equation. When, however, the hypochlorite solution was acidified with acetic acid before titration, the results were found to be different and indicated the completion of the reaction as shown by Equation 2, where eight equivalents of chlorine are consumed in the complete oxidation of one mole of sodium thiosulfate. No record was available to show that this reaction had ever been tested out in an acetic acid solution.

EXPERIMENTAL DATA

PREPARATION OF SOLUTIONS. The strength of the sodium thiosulfate solution was so adjusted that 50 cc. of the thiosulfate reacted with 6.25 cc. of a 0.1 *N* iodine solution when using starch as an indicator.

The strength of the arsenite solution was so adjusted that it reacted with equivalent quantities of a 0.1 *N* iodine solution when using starch as an indicator.

The reaction of sodium thiosulfate on a hypochlorite solution was determined (*a*) by titrating an acetic acid solution of sodium hypochlorite with a 0.1 *N* sodium thiosulfate solution and using starch–potassium iodide paper as an outside indicator; (*b*) by adding an excess of potassium iodide to an acetic acid solution of sodium hypochlorite, and titrating the liberated iodine with the same thiosulfate solution used in (*a*), while using starch solution as an internal indicator.

Fifty cubic centimeters of chlorine solution required in (*a*) 2.88 cc. and in (*b*) 23.05 cc. of sodium thiosulfate. Therefore, 23.05/2.88 equals 8.003 equivalents of chlorine reduced per equivalent of iodine reduced by sodium thiosulfate from an acetic acid solution of a hypochlorite.

Several hundred analyses of solutions of sodium and calcium hypochlorite, with chlorine concentrations varying from 25 parts per million to 1.25 per cent of available chlorine, have been made by the use of this method and the results have been found to check within an error of ±0.2 per cent of the available chlorine as determined by the arsenic trioxide method. Tests have been made at temperatures from 10° to 35° C. and with concentrations of acetic acid from barely acidic to 33.3 per cent glacial acetic acid. At high temperatures and with a large excess of acetic acid, there is a loss of chlorine before titration, but the reaction goes to completion to form the sulfate, as has been shown by checking the concentration of available chlorine with a standard arsenic solution.

Tables I, II, and III are submitted to show the effect of acetic acid, strong alkalies, and high temperatures, respectively, on the reaction.

TABLE I. EFFECT OF ACETIC ACID

(Reaction temperature, 25° C. Indicator, starch–potassium iodide paper. Concentration of hypochlorite solution, 20 cc. equals 19.16 cc. of 0.1 *N* arsenite solution.)

Hypochlorite Solution Used	10 Per Cent Acetic Acid Solution Added	0.1 *N* Sodium Thiosulfate	Reaction to Litmus Before titration	Reaction to Litmus After titration
Cc.	*Cc.*	*Cc.*		
20	0	36.30	Basic	Basic
20	0.1	38.00	Basic	Basic
20	0.2	39.60	Basic	Basic
20	0.3	42.00	Basic	Basic
20	0.4	45.05	Basic	Basic
20	0.5	49.20	Basic	Basic
20	0.6	53.60	Basic	Basic
20	0.7	19.12	Acidic	Acidic
20	0.8	19.14	Acidic	Acidic
20	0.9	19.13	Acidic	Acidic

TABLE II. EFFECT OF STRONG ALKALIES

(Reaction temperature, 25° C. Indicator, starch–potassium iodide paper. Concentration of hypochlorite solution, 20 cc. equals 18.40 cc. of 0.1 *N* arsenite solution.)

Hypochlorite Solution	Treatment of Hypochlorite Solution before Titration	0.1 *N* Sodium Thiosulfate
Cc.		*Cc.*
20	1 cc. of 1% NaOH added	34.25
20	10 cc. of 1% NaOH added	26.30
20	1 cc. of 5% Na_2CO_3 added	35.10
20	10 cc. of 5% Na_2CO_3 added	35.00
20	1 cc. of 5% $NaHCO_3$ added	42.40
20	10 cc. of 5% $NaHCO_3$ added	56.50

Table III. Effect of High Temperatures

(Indicator, starch–potassium iodide paper.)

Hypochlorite Solution		10 Per Cent Acetic Acid Added	0.1 *N* Sodium Thiosulfate	0.1 *N* Sodium Arsenite
Cc.	° *C.*	*Cc.*	*Cc.*	*Cc.*
50	10	2	25.58	25.60
50	15	2	25.51	25.56
50	20	2	25.50	25.55
50	25	2	25.51	25.52
50	30	2	25.46	25.50
50	35	2	25.40	25.45

Discussion of Results

The reaction of sodium thiosulfate on a hypochlorite is influenced by the alkalinity of the solution, as is shown by Tables I and II. As the alkalinity is decreased, the amount of thiosulfate required for the destruction of the chlorine is increased until the solution is made acidic, when a different reaction takes place and goes to completion to form the sulfate according to Equation 2.

Diénert and Wandenbulcke (*2*) state that the alkalinity of a hypochlorite solution after titration with sodium thiosulfate is the same as the alkalinity of the hypochlorite solution determined after the destruction of the chlorine with hydrogen peroxide. This is not in conformity with the results obtained in this laboratory and the following explanation concerning the mechanism of the reaction is offered: When Reaction 1 takes place with a hypochlorite solution it is correctly written as:

$$2Na_2S_2O_3 + NaOCl + H_2O \longrightarrow Na_2S_4O_6 + 2NaOH + NaCl \quad (3)$$

where one equivalent of alkali is liberated per mole of sodium thiosulfate consumed. Under the same conditions Reaction 2 should be written:

$$Na_2S_2O_3 + 4NaOCl + H_2O \longrightarrow 4NaCl + Na_2SO_4 + H_2SO_4 \quad (4)$$

where two equivalents of acid are liberated per mole of sodium thiosulfate consumed. Adding Equations 3 and 4 we get Equation 5 which is a neutral reaction.

$$3Na_2S_2O_3 + 5NaOCl \longrightarrow Na_2S_4O_6 + 5NaCl + 2Na_2SO_4 \quad (5)$$

From these reactions we may conclude:

1. If Reaction 3 takes place in excess of Reaction 4, the alkalinity of the hypochlorite solution will be increased.
2. If Reaction 4 takes place in excess of Reaction 3, the alkalinity of the hypochlorite solution will be decreased.
3. If Reactions 3 and 4 take place to form Reaction 5, the alkalinity of the solution will not be affected.

In all cases of titrating hypochlorite solutions which contain sodium hydroxide or carbonate, with sodium thiosulfate, the amount of thiosulfate consumed indicates that Reaction 4, although not quantitative, is the predominating one. With hypochlorite solutions that contain an excess of bicarbonate or are neutral in reaction, the thiosulfate consumed exceeds the theoretical amount required for Equation 5, and an alkaline reaction is produced. This accounts for the fact that when a neutral or an alkaline solution of a hypochlorite is reduced with sodium thiosulfate, the resulting solution is always alkaline, and explains why in some cases the alkalinity after titration with sodium thiosulfate is the same as the alkalinity of the solution after the chlorine has been destroyed with hydrogen peroxide.

In no case was the precipitation of sulfur observed or sulfur dioxide or hydrogen sulfide liberated when sodium thiosulfate was added to either an acetic acid or an alkaline solution of a hypochlorite. The experiments as here conducted have been with solutions of alkaline hypochlorites and with solutions of hypochlorites containing a small excess of acetic acid and consequently hypochlorous acid, while chlorine solutions as previously referred to may have in some instances implied solutions of chlorine in water which contained hydrochloric acid in equivalent proportions to the hypochlorous acid. In this case the precipitation of sulfur and the formation of sulfur dioxide are to be expected. Very dilute hydrochloric or sulfuric acids act like acetic acid, but with these acids there is danger of a loss of free chlorine and also of the formation of sulfur and sulfur dioxide.

Chlorates which may be present in hypochlorites do not interfere with the reaction of sodium thiosulfate in an acetic acid solution of a hypochlorite and this method gives a measure of the available chlorine only (*5*).

In processes where sodium thiosulfate is used as an antichlor, it is believed that the amount of thiosulfate required for the destruction of the chlorine can be calculated, and that a great saving can be made in the amount of thiosulfate by properly controlling the hydrogen-ion content of the solution and forcing the antichlor reaction to completion to reduce eight equivalents of chlorine per mole of sodium thiosulfate.

Method of Analysis

Reagents Required. 0.1 *N* sodium thiosulfate, starch–potassium iodide paper, and dilute acetic acid (10 per cent glacial acetic).

Preparation of 0.1 *N* Sodium Thiosulfate Solution. This solution is prepared by dissolving slightly over 3.1025 grams of the crystallized salt per liter of solution and adjusting the concentration so that it reacts with equivalent volumes of an iodine solution containing 1.5865 grams of pure iodine per liter of solution. The solution is then 0.1 *N* to chlorine when used for titrating an acetic acid solution of a hypochlorite and is 0.0125 *N* to iodine.

Method. The hypochlorite is diluted with water to contain approximately 0.1 per cent of available chlorine. Fifty cubic centimeters of this solution are pipetted into an Erlenmeyer flask and dilute acetic acid is added until a drop of the solution, when taken out on a glass rod, shows an acid reaction to litmus before the litmus is completely bleached. The thiosulfate solution is then run into the hypochlorite solution from a buret, a few cubic centimeters at a time, until a drop of the reacting solution fails to give a chlorine reaction with starch–potassium iodide paper. A second or third titration may be necessary in order to obtain the exact end point. The concentration of available chlorine in the original hypochlorite is then calculated from the amount of dilution and the volume of sodium thiosulfate used.

Summary

Experiments conducted in this laboratory have demonstrated that sodium thiosulfate, when added to a dilute acetic acid solution of a hypochlorite, is completely oxidized to the sulfate and that eight equivalents of chlorine are used per mole of sodium thiosulfate. The reaction can be used as a quantitative method for determining available chlorine in a hypochlorite. The sodium thiosulfate solution is standardized by titrating against an iodine solution of known concentration. The end point of the reaction is determined by the use of starch–potassium iodide paper as an external indicator. When working at laboratory temperatures of from 20° to 25° C., this method gives results which check with those obtained when using a standard arsenite solution for reducing the chlorine.

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Precise Determination of Calcium, Magnesium, and Phosphorus in Evaporated Milk

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THE relation of the heat stability of evaporated milk to the minerals or salts found in it has been the subject of several experiments. There is considerable difference of opinion in the interpretation of these experiments. This relation is of commanding interest because the range between the temperature necessary to sterilize the evaporated milk and the temperature at which the milk will form an objectionable curd is narrow, and because the allowable temperature can sometimes be raised by adding very small amounts of mineral salts to the milk.

Sommer and Hart (*4*) conclude that the milk salts are the main factor in determining the heat coagulation of evaporated milk and that the error in the contradictory conclusion of Rogers, Deysher, and Evans (*2*) is explained by the fact that their analytical results may involve errors larger than the amounts of added salts needed to affect the heat stability of the milk. The salts most satisfactory for increasing the heat stability of most samples of milk contain either citrates or phosphates, but calcium or magnesium salts are needed in some samples. Samples improved by the polybasic acids are made worse by the polyvalent bases and vice versa. The present paper describes an effort to increase the precision of analysis to a point comparable with the amounts of salts added to control the heat stability of milk.

It seemed likely that the error due to loss of moisture while weighing out the sample might be large compared with the precision sought. The determinations studied are, therefore, those which can be made on a single sample. Calcium, magnesium, and phosphorus have been determined by a procedure including only steps described by Scott (*3*) or the Association of Official Agricultural Chemists (*1*). No effort has been made to check the exact composition of the products

Table I. Minerals in Evaporated Milk

Sample		Ash	Calcium		Magnesium		Phosphorus	
				Ratio[a]		Ratio[a]		Ratio[a]
		%	%		%		%	
A_1	1	1.63674	0.28971	0.17700	0.02629	0.016063	0.21314	0.13022
	2	1.63622	0.28924	0.17677	0.02602	0.015903	0.21300	0.13018
	3	1.63693	0.28934	0.17676	0.02650	0.016189	0.21304	0.13015
	Av.	.....	0.28943	0.17684	0.02627	0.016052	0.21306	0.13018
	e[b]	.....	19	10	17	9.9	5	3
	f[c]	.....	6.6	5.6	6.5	6.2	2.4	2.3
B_1	1	1.56481	0.26341	0.16833	0.02275	0.014538	0.20859	0.13330
	2	1.56443	0.26321	0.16825	0.02241	0.014547	0.20880	0.13347
	3	1.56462	0.26325	0.16825	0.02276	0.014545	0.20874	0.13341
	Av.	.....	0.26329	0.16828	0.02264	0.014543	0.20871	0.13339
	e[b]	.....	8	4	15	4	8	6
	f[c]	.....	3.0	2.4	6.6	2.8	3.8	4.5
C_1	1	1.59387	0.28186	0.17684	0.02459	0.015428	0.20206	0.12677
	2	1.59403	0.28166	0.17670	0.02421	0.015188	0.20217	0.12676
	3	1.59379	0.28164	0.17671	0.02404	0.015084	0.20210	0.12680
	Av.	.....	0.28172	0.17675	0.02428	0.015233	0.20211	0.12678
	e[b]	.....	9	6	21	13.0	4	2
	f[c]	.....	3.2	3.4	8.6	8.5	2.0	1.5
A_2	1	1.60477	0.26874	0.16746	0.02599	0.016195	0.23137	0.14418
	2	1.60484	0.26911	0.16769	0.02602	0.016213	0.23120	0.14406
	3	1.60455	0.26903	0.16767	0.02587	0.016123	0.23132	0.14417
	Av.	.....	0.26896	0.16761	0.02596	0.016177	0.23130	0.14414
	e[b]	.....	15	10	6	3.6	6	5
	f[c]	.....	5.6	5.9	2.3	2.2	2.6	3.5
B_2	1	1.55991	0.25487	0.16339	0.02341	0.015007	0.23026	0.14761
	2	1.55933	0.25451	0.16322	0.02323	0.014898	0.23004	0.14753
	3	1.56004	0.25463	0.16322	0.02347	0.015044	0.22988	0.14736
	Av.	.....	0.25467	0.16328	0.02337	0.014983	0.23006	0.14750
	e[b]	.....	13	8	8	6.0	13	9
	f[c]	.....	5.1	4.9	3.4	4.0	5.6	6.1
C_2	1	1.59111	0.26694	0.16777	0.02616	0.016441	0.22206	0.13956
	2	1.59143	0.26659	0.16752	0.02671	0.016784	0.22221	0.13963
	3	1.59091	0.26714	0.16792	0.02651	0.016663	0.22218	0.13966
	Av.	.....	0.26689	0.16774	0.02646	0.016629	0.22215	0.13962
	e[b]	.....	20	14	20	12.6	6	4
	f[c]	.....	7.5	8.3	7.6	7.6	2.7	2.9
A_3	1	1.59760	0.29141	0.18241	0.02541	0.015905	0.21491	0.13452
	2	1.59773	0.29177	0.18262	0.02561	0.016029	0.21447	0.13423
	3	1.59747	0.29180	0.18266	0.02575	0.016119	0.21459	0.13433
	Av.	.....	0.29166	0.18256	0.02559	0.016018	0.21466	0.13436
	e[b]	.....	17	10	12	7.5	17	11
	f[c]	.....	5.8	5.5	4.7	4.7	7.9	8.2
C_3	1	1.59126	0.27867	0.17513	0.02541	0.015968	0.20659	0.12983
	2	1.59150	0.27823	0.17482	0.02571	0.016155	0.20627	0.12961
	Av.	.....	0.27845	0.17497	0.02556	0.016062	0.20643	0.12972
	e[b]	.....	22	15	15	9.3	16	11
	f[c]	.....	7.9	8.6	5.9	5.8	7.8	8.2
A_4	1	1.58881	0.28459	0.17912	0.02526	0.015899	0.20983	0.13207
	2	1.58907	0.28433	0.17893	0.02578	0.016223	0.21009	0.13221
	Av	.....	0.28446	0.17901	0.02552	0.016007	0.20996	0.13214
	e[b]	.....	13	8	26	10.6	13	7
	f[c]	.....	4.6	4.5	10.2	6.7	6.2	5.3
C_4	1	1.58476	0.28386	0.17912	0.02523	0.015920	0.20634	0.13020
	2	1.58522	0.28422	0.17929	0.02509	0.015827	0.20586	0.12986
	Av.	.....	0.28404	0.17921	0.02516	0.015873	0.20610	0.13003
	e[b]	.....	18	8	7	4.6	24	17
	f[c]	.....	6.3	4.5	2.8	2.9	11.6	13.0

[a] Ratio of per cent of element to per cent of ash.
[b] $10^5 \times$ the average total deviation as per cent of sample.
[c] $10^5 \times$ the average relative deviation as a fraction of the constituent.

isolated and weighed, but it is assumed that the composition of each product is constant, at least to the degree of reproducibility obtained. Small constant errors in the composition of a product would not affect the comparative amount in different samples.

The hope of increased precision rested on two refinements of manipulation—the close control of temperature during the ashing of the milk and during the ignition of precipitates, and the use of a balance with high precision and large capacity. A No. 10 Troemner balance was used. The sensitivity was increased by means of an auxiliary scale and telescope, so that weights could be read to 2 micrograms. The reliability of these weighings was at least within 10 micrograms. The temperature of the muffle furnace was recorded and controlled within about 2° C. by a Leeds & Northrup self-operating potentiometer and a calibrated iron-constantan thermocouple.

The beakers used during the formation and digestion of precipitates were of Pyrex glass. Platinum dishes were used for all ashing and ignition processes. Before weighing an empty platinum dish, it was slowly warmed in 6 *N* hydrochloric acid to a temperature slightly below boiling. The dish was then rinsed with water and ignited to constant weight at the same temperature as that at which the next ash was to be ignited.

Determinations

Into a weighed platinum dish about 50 grams of well-mixed evaporated milk were pipetted. The dish with contents was then weighed to 0.1 mg. and heated in an electric oven at 120° C. until the contents were dry and partly charred. The dish was then placed in a cool electric muffle furnace and heated to 550° C. in the course of 1.5 to 2.5 hours. Heating at this temperature was continued until constant weight was obtained, usually from 14 to 20 hours. The dish with ash was then weighed to 2 micrograms. It was demonstrated that at temperatures of 490° C. or lower the ash would not become white in 72 hours. At temperatures above 560° C. the ash continued to lose weight for 72 hours. It was not possible to secure satisfactory checks at either too high or too low temperatures.

The isolation of calcium involved precipitation as a mixture of oxalate and phosphate, ashing at 570° C., conversion to a mixture of carbonate and phosphate, drying at 150° C., and weighing. This weighed mixture was dissolved in hydrochloric acid, and calcium phosphate precipitated from the solution and heated to constant weight at 535° C. The following calculations could then be made: weight of calcium carbonate, weight of calcium in carbonate, weight of calcium in phosphate, total weight of calcium, and weight of phosphorus in calcium phosphate.

Magnesium was removed as phosphate from the solution of ash from which calcium had been isolated, heated to constant weight at 585° C., and weighed as magnesium pyrophosphate. The weight of magnesium and the weight of a second fraction of phosphorus were calculated from this weight.

The remaining phosphorus was isolated with magnesia mixture, ignited at 585° C., and weighed as magnesium pyrophosphate.

The results are shown in Table I. The three brands of milk used are designated as A, B, and C, the different tins of each brand being shown by the subscripts.

Discussion of Results

The question whether or not there may be a serious loss of moisture in weighing the sample is answered by comparing the deviations in the per cent and ratio columns. For each of the three elements determined, the average relative deviation (f) as per cent of sample, and as ratio to ash, is between 5 and 6 in the fifth place. Since the deviation of ratios is not much less than the deviation of per cent we conclude that the weighing of samples involves no serious loss of water. This opens the way for the development of a correspondingly precise method for the determination of citrates.

The deviation (e) of per cent corresponds to the addition of less than 2 parts of the element per million parts of the evaporated milk. Analysis with corresponding precision of all the constituents affecting heat stability should settle the question whether or not the amounts of various minerals are an adequate criterion of heat stability. If citrates are the only additional important constituent, the task does not look impossible.

A comparison of the amounts of the different significant salts will be much more valuable when data on citrates are available. In the meantime it may be observed that the relation of calcium to magnesium, the relation of the sum of these to phosphorus or to ash, and the relation of phosphorus to ash, all vary by about 10 per cent. There seems to be no systematic order in these variations.

Conclusion

If a sensitive balance of large capacity is used, and if the temperatures for ashing the milk and for igniting the precipitates are properly chosen and closely maintained, it is possible to determine the calcium, magnesium, and phosphorus content of evaporated milk with a variation of less than 2 parts per million. Addition of one or more of these minerals in amounts up to about 10 parts per million frequently improves the quality of the product.

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Device for Holding Electrodes during Electrometric Titrations

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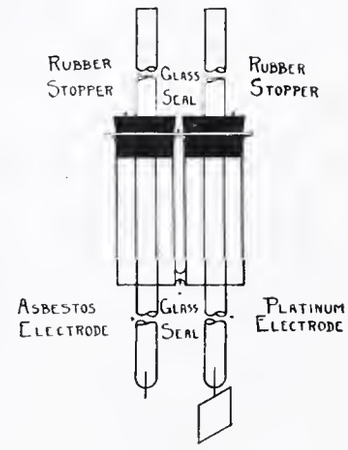
A very useful and convenient piece of apparatus for use with the asbestos[1] or similar electrodes is shown in the accompanying sketch. This device is particularly useful when making electrometric titrations, as it always insures uniform spacing of the electrodes and offers a compact, rigid mounting for them. This mounting allows the operator greater freedom while titrating and also readily lends itself for rapidly changing the electrodes.



The apparatus can very readily be made by the amateur glass blower from two 1.25-cm. (0.5-inch) test tubes which have been cut off 3.2 cm. (1.25 inches) below the lip and sealed together in the manner shown.

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A New Method for Measuring Corrosion of Metals

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In studying the action of corrosive agents it is usual to apply some gravimetric method of measuring the material lost from a test piece, either by subjecting the test piece to the action of the corrosive agent for a certain length of time and weighing it before and after the test, or by determining analytically the amount of metal dissolved in the corrosive agent.

To obtain anything like reliable results from either of these methods a fairly intensive corrosion has to be effected. As this in many instances involves too much time for practical purposes, accelerated corrosion tests are often applied—for instance, by working at a higher temperature or with a higher concentration of the corrosive agent than is usual in practice. It is well known, however, that such accelerated tests hardly ever give strictly comparable results, and in many cases the conditions and results of the test deviate so far from what takes place normally that the conclusions drawn therefrom are entirely wrong.

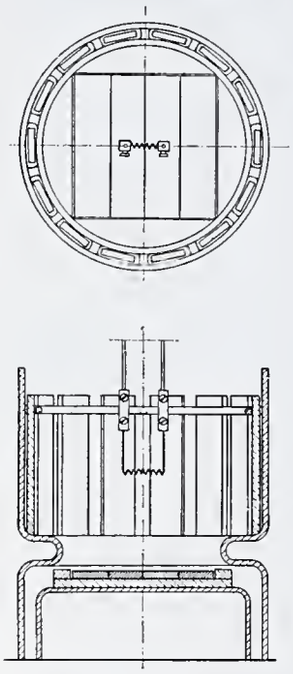

Figure 1. Container for Glass Plaques

It is therefore of great importance to devise a method whereby even the slightest corrosion can be measured quantitatively with great accuracy under normal conditions and within a reasonable time. Such a method has now been developed by sublining extremely thin layers of metal (about 8×10^{-6} cm. thick) on glass plaques in high vacuum and measuring their thickness before and after subjecting them to corrosive action, the measurements being made by determining the coefficient of the light-transmissibility of the metal-coated plaques. Owing to the high absorption coefficient of metals, with an optical apparatus of great precision it is possible to measure a change in thickness of even one atomic diameter. In the author's tests such a high degree of accuracy was not required, so that a simpler apparatus sufficed, with which he was able to measure differences of 5 atomic diameters.

This method has been found to be very useful for measuring the degree of aggressiveness of a liquid or gas which is only slightly corrosive, as may be necessary in practice—for instance, in cases where a large quantity of liquid flows along metal parts where even the slightest wear may have undesirable consequences, even leading to a serious interruption of the work As an example may be mentioned the fuel pump of a solid-injection Diesel engine.

Preparation of Test Plates

The maximum thickness of a metal layer which can transmit light to a measurable degree is of the order of 10^{-5} cm. or less. Such a layer can be made by subliming the metal in high vacuum on a base of transparent material (glass), and if the necessary precautions are taken during the sublimation the metal layers adhere so well to the base that they can safely be heated in a liquid for a long time without risk of becoming detached.

The glass plates (dimensions $4 \times 1 \times 0.2$ cm.) were first cleaned with nitric acid, washed with soapsuds, and rinsed first with tap water and then with distilled water; they can also be cleaned with chromic acid and rinsed with distilled water. Fourteen of these cleaned plates were placed upright in a glass container (Figure 1) and four more laid on the bottom, the container then being ready to be placed in an evaporation bell (Figure 2).

The bell was 17 cm. high and 9 cm. in diameter, closed at the bottom with a ground-glass plaque 2 cm. thick by means of a little vacuum grease. At the top a ground stopper was fitted in, through which a fine tungsten coil mounted on two nickel conducting wires could be passed down into the bell. The bell was connected by a tube at the side to a mercury diffusion pump, with a liquid nitrogen trap to prevent the mercury vapor from getting into the bell. The diffusion pump was connected up to a mercury-vapor jet pump, for which the required low vacuum was drawn by a rotary oil pump.

A weighed piece of cleaned metal was then put into the tungsten coil, the container with the glass plates placed in the bell, and the apparatus exhausted. (The tungsten filament was lowered to a level just opposite the centers of the glass plates, at an average distance of about 3 cm. from the centers.) A few minutes after the pumps had been started, liquid nitrogen was supplied to the cooling vessel, and after waiting a few more minutes the current for the tungsten filament was switched on (from experience it was known that with the assembly used a high vacuum, 10^{-4} mm. of mercury, was obtained within a few minutes). The heating current was derived from a 36-volt storage battery, adjustment being made by means of a resistance so as to obtain a favorable rate of evaporation. The proper working temperature, in general, is in the neighborhood of the melting point of the metal used. The coil should be heated slowly, allowing plenty of time for the gases liberated to be pumped off; if heating takes place too quickly there is danger of particles of the metal flying off from the tungsten filament, or the gases may not be pumped off quickly enough, thus spoiling the vacuum.

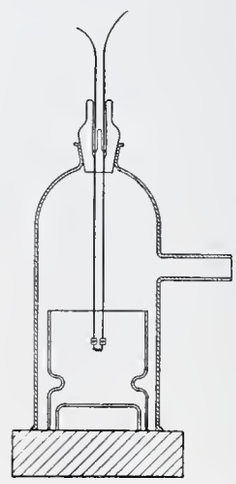

Figure 2. Evaporation Bell for Room Temperature

As soon as the piece of metal in the filament had entirely disappeared, the current was switched off. After cooling, air was admitted, the bell opened, and the container with the metal-coated glass plates removed. The plates were then marked and those not required for immediate use were kept immersed in kerosene previously treated with sodium. (It had been found that copper and zinc kept under kerosene not so treated showed the beginning of corrosion after a few weeks.)

For making plaques with a layer of iron of about 4 to 8×10^{-6} cm. thickness, a piece of florists' iron wire of about 10^{-2} gram was used. Preferably, pure metals are used to insure good reproducibility, and in the author's tests for the comparison of various oils it was also desirable to use pure metals rather than alloys, which naturally have to differ in composition according to the purpose for which they are employed. Nevertheless, for the author's own information he also examined some alloys and did not encounter any great difficulties.

Iron and Copper. The sublimation of iron and copper presented no difficulties, smooth and glossy metallic layers being obtained on the glass plates.

Zinc. In the case of this metal difficulties were encountered. At room temperature the zinc did not precipitate uniformly on the glass plates, because at room temperature zinc is so volatile that the atoms have very little chance of adhering to the glass. An attempt to remedy this by increasing the density of incidence of the zinc atoms (by more rapid heating) did not yield the desired result, but it was found that by cooling the plates smooth and glossy layers of zinc could be obtained. This involved the use of a different type of evaporation bell and holder for the glass plates (Figure 3).

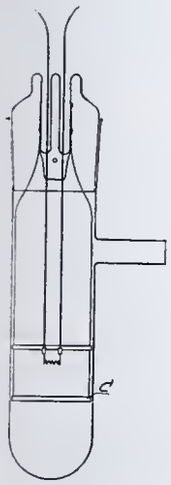

Figure 3. Evaporation Bell for Low Temperature

C, container for glass plaques

For these tests with zinc a nickel holder was used, being suspended from the ground joint in the neck of the bell, so that the part of the glass wall of the bell that has to be cooled is nowhere in contact with metal or glass, which would involve the danger of the bell's breaking; cooling was done with liquid nitrogen.

With zinc an interesting phenomenon was noticed which shows the mobility of the atoms on the glass surface: The zinc precipitated in floccular form on one part of the plate, the rest of the plate remaining free, this being attributable to an accidental local conglomeration of condensation nuclei. After the sublimation had ended, the zinc was found to be moving along the glass surface, ultimately covering the whole of the plate, also at the back. The spreading velocity of the zinc could be substantially increased by heating the plate by radiation from the bell (all being done in high vacuum) this being heated by means of hot air from a hair-drying machine.

Influence of the Vacuum. In preparing the metal-plated test plaques care must be taken to use the right vacuum. To obtain smooth, glossy, and reflective metal layers it is essential that the metal atoms should not collide on their way; they should pass direct from the molten metal to the glass and stick there. The mean free path for the atoms should therefore be of the order of the distance between the filament coil and the glass plate, or greater, which corresponds to pressures of a few times 10^{-4} mm. of mercury or lower. If there is a considerable chance for collisions (pressures of the order of 10^{-2} mm. of mercury), the metal particles will partially agglomerate on the way, resulting in a layer that is not coherent and has a dull black appearance, as a consequence of diffuse reflection and accompanying absorption of light. At higher gas pressures the metal and the tungsten coil oxidize in the air.

Transmissibility of Metal Layers to Light

The transmissibility of the metal layers was measured optically by means of the apparatus shown diagrammatically in Figure 4, all the parts being mounted on a Zeiss rail to facilitate centering.

The source of light was an incandescent lamp with milk-glass bulb fitted in a case with open front. The light first passed through a tank filled with dilute copper sulfate solution (absorbing the infra-red rays and thus preventing undesirable heating of the plaque), then through a plate of photographic red glass (the region of visible spectrum transmitted thereby being narrowed down from 5900 Å. to infra-red, average 6200 Å., so that the absorption coefficient and the refractive index of the metal could be considered as constants), and finally through a milk-glass plate (making the illumination more uniform).

The plate was fastened in a holder with a spring and placed in front of the top half of a rectangular opening in diaphragm *D*. The image of this rectangular opening and the plaque was obtained through two lenses of the same focal distance (the two halves of a spectacle-glass, 8 *D*, placed at a short distance one above the other) which could be brought sufficiently close together to produce adjacent images on a focusing screen. Each lens was diaphragmed, leaving a rectangular opening 1.20 × 2 cm., while the lower lens could be further diaphragmed, leaving a smaller, triangular opening adjustable according to a scale. From the position of a mark on the fixed diaphragm with respect to the scale, the free surface of the lens could be calculated by employing a conversion graph (a small lamp was mounted to illuminate the scale, and also a magnifying glass to make it easy to read the position of the mark).

Each of the images cast on the focusing screen consisted of a dark strip, corresponding to the part of the opening in the first diaphragm, *D*, covered by the plaque, which, being coated with metal, was only slightly translucent, and a light strip corresponding to the uncovered part of the first diaphragm opening. By adjusting the distance between the two lenses the images could be made to touch, so that four adjoining strips, dark-light-dark-light, became visible on the screen. The two extreme strips were then diaphragmed off and the other two strips brought to equal strength by adjusting the triangular diaphragm opening until their line of demarcation disappeared. With a uniform illumination the ratio of the lens surface remaining after diaphragming to the total surface of the other lens is equal to the fraction of incident light penetrating the metal-coated plaque—i. e., it is equal to the transmissibility of the plaque. The position of the index mark on the fixed diaphragm behind the lenses with respect to the scale on the movable diaphragm was then noted and the corresponding transmissibility of the metal layer was read from the conversion graph mentioned above.

It is not, strictly speaking, the transmissibility of the metal layer alone that is thus found, as the beam of light is also slightly weakened by reflection at the boundary between air and glass on the noncoated side of the plaque. The same reflection also occurs, however, when the determination is repeated with the same plaque after it has been subjected to the action of the corrosive agent, so that this does not affect the difference in transmissibility. Neither are the determinations affected by the fact that after corrosion the metal layer is less reflective than before, since the measurements are made in diffuse light.

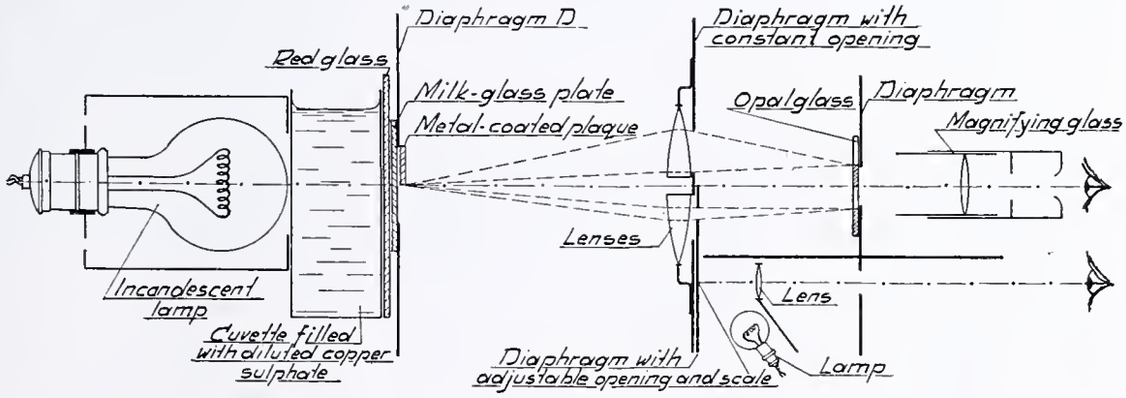

Figure 4. Apparatus for Transmissibility Measurement

The question has been raised of the interference of protective films on light transmission where the film is opaque and firmly attached to the metal and where some of the passive films may be as thick as the test metal to be used. The author has invariably met with corrosion products that could easily be removed and were practically transparent or at most pale yellow in color. To reduce as much as possible the interference of films that might have been left behind, the ab-

sorption of the layer of metal was determined in red light, where, as may be concluded from the pale yellow color of the corrosion products, their absorption was a minimum.

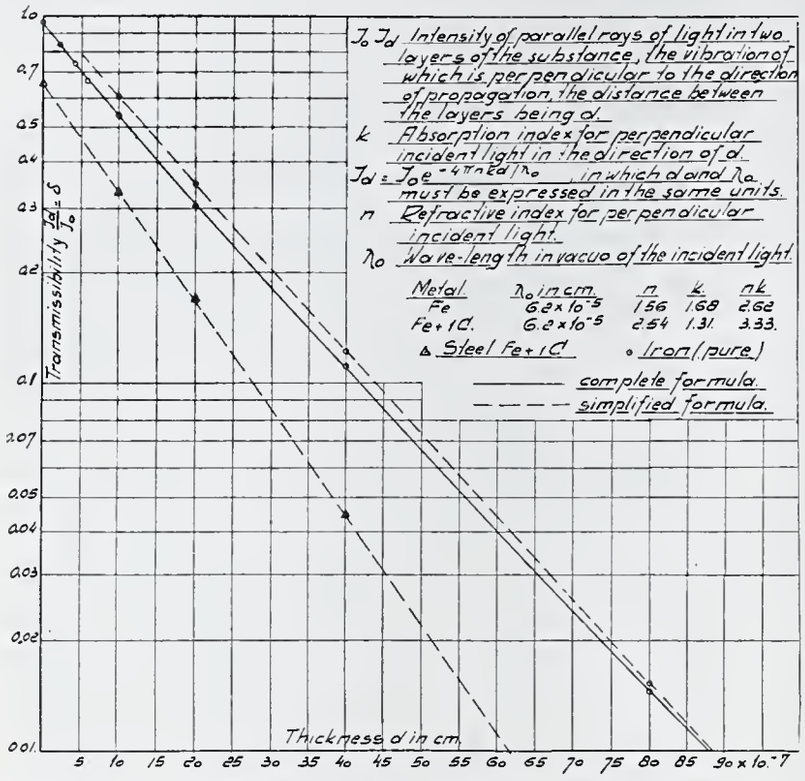

FIGURE 5. TRANSMISSIBILITY OF LAYERS OF IRON AND STEEL AS A FUNCTION OF THICKNESS

It must be recalled that to cause interference the coefficient of absorption of the corrosion products must be of the same order of magnitude as that of the metal, which will very rarely be the case. A substance so strongly absorbent that a 10^{-3}-cm. (10 μ) layer is quite opaque (transparency less than 0.0001), lets through 95 per cent of the light falling on a layer of 5×10^{-6} cm. (apart from reflection).

If a substance were found that could not be removed from the metal and that had an absorption of the same order of magnitude as the metal layer, the method could still be used if the coefficient of absorption differed from that of the metal. By allowing a thin layer of metal to corrode away entirely, the absorption of the equivalent layer of the substance affected may be determined—i. e., the layer, d^1, of the corrosion product formed by complete corrosion of a layer of metal, d.

By taking layers of different thicknesses, the connection between absorption and the equivalent thickness of a layer may be experimentally established.

From the transmissibility of the plaque its thickness is also found graphically by means of the known absorption coefficient of the metal layer.

The exact connection between the thickness of the layer and the optical constants of the metals should, however, be dealt with at some length here. With the simple measuring apparatus described above, the thickness of the metal layers could be determined with an accuracy of 10^{-7} cm., which was more than sufficient for the purpose the author had in view—viz., the examination of gas oils, in order to investigate the reproducibility of corrosion by gas oils.

OPTICAL CONSTANTS OF THIN METAL LAYERS

The transmissibility of a metal layer of any thickness can be calculated by means of the electromagnetic theory of light. For a thick layer the weakening of the light due to the presence of the layer can be divided into two factors, one representing the weakening by absorption and the other the weakening by reflection against the metallic mirror. With thin layers this division is no longer possible, so that only the total transmissibility of the layer can be spoken of. The general relation between the intensity, $I(d)$, of the light which has passed through an absorbing layer with a thickness of d (absorption coefficient k and refractive index n) and the original intensity, $I(o)$, at perpendicular incidence from air on metal and subsequently on glass (refractive index n') is:

$$I(d)/I(o) = 16\,n'(n^2 + n^2k^2)/\left\{ e^{\frac{4\pi nkd}{\lambda}} [n^2k^2 + (n+1)^2] [n^2k^2 + (n+n')^2] + e^{\frac{-4\pi nkd}{\lambda}} [n^2k^2 + (n-1)^2] [n^2k^2 + (n-n')^2] - 2[(n^2k^2 + n^2)^2 - n^2(1 + n'^2) + n'^2 - n^2k^2(n'^2 + 4n' + 1)] \cos\frac{4\pi nd}{\lambda} + 4nk(n'+1)(n^2 + n^2k^2 - n') \sin\frac{4\pi nd}{\lambda} \right\} \quad (1)$$

In this formula λ is the wave length of the light used (*4*).

If the layer is very thick (d great), the term

$$e^{\frac{4\pi nkd}{\lambda}} [n^2k^2 + (n+1)^2] [n^2k^2 + (n+n')^2]$$

dominates in the denominator, so that $I(d)$ should be written as

$$I(d) = I(o) \frac{16n'(n^2 + n^2k^2)}{[n^2k^2 + (n+1)^2][n^2k^2 + (n+n')^2]} \times e^{\frac{-4\pi hkd}{\lambda}} \quad (2)$$

The intensity $I(d)$ is now determined by two factors, the first of which does not contain the thickness of the plaque, (weakening by reflection), while in the second the thickness of the plaque occurs in the exponent (weakening by absorption). Equation 2 is so much simpler than 1 that there are certain advantages in using layers of such a thickness that 2 can be applied. For if we plot $I(d)/I(o)$ logarithmically against the thickness of layer, the second formula is repre-

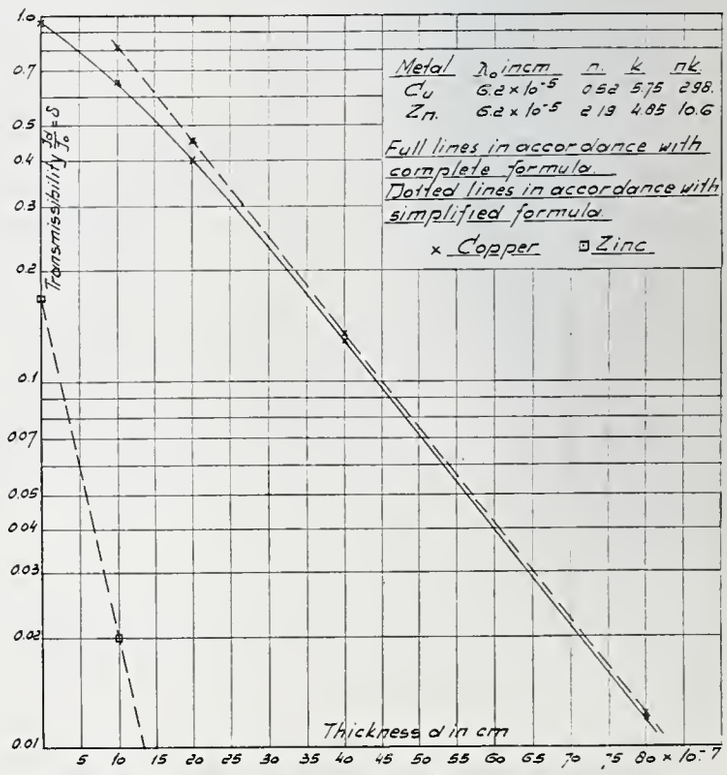

FIGURE 6. TRANSMISSIBILITY OF LAYERS OF COPPER AND ZINC AS A FUNCTION OF THICKNESS

sented by a straight line. It has been found that for the metals used by the author layers of about 3×10^{-6} cm. can be considered thick in the sense of Equation 2. In Figures 5 and 6 Equations 1 and 2 have been plotted graphically [$I(o) = 1.00$] for iron and copper with the values of n and k stated for these metals (*1*).[1] For steel (Fe + 1 C) and for zinc only Equation 2 has been plotted. For the calculations the author has taken $n' = 1.50$ (the refractive index for glass). For $d = 3 \times 10^{-6}$ or more, the curves for Equations 1 and 2 are practically parallel. For such thicknesses Equation 2 can therefore be used instead of Equation 1 to measure differences in thickness. When preparing the glass plaques the author invariably saw to it that the minimum thickness of 3×10^{-6} cm. was exceeded, so that Equation 2 could be used.

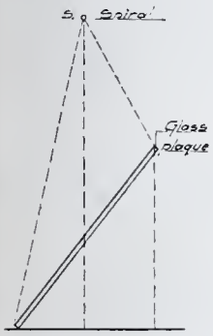

FIGURE 7. OBLIQUE GLASS PLAQUE FOR MEASUREMENT OF n AND k

There is another reason why it is desirable always to use metal layers thicker than about 3×10^{-6} cm. The optical constants of the metals (n and k) are to a great extent dependent on the crystal lattice in which the metal atoms are arranged. Now in a monoatomic metal layer the metal atoms are in conditions quite different from those in a crystal lattice. This lattice is gradually built up in proportion as the number of atom layers increases, so that in general the optical constants for very thin layers may be expected to depend on the thickness of the layer, and to differ from the constants of a solid piece of metal. Only by measurement can it be established at what thickness of layer these deviations become perceptible—i. e., become of the order of 1 per cent. Various investigators have occupied themselves with this dependence of n and k on the thickness of layer d. Leaving out of consideration the old, highly uncertain determinations from the time preceding the development of the high-vacuum practice, the author found that for none of the metals examined were any deviations noticed for layers thicker than 3×10^{-6} (*4*).

With thinner layers n and k were sometimes found to vary very rapidly (Ag, Pt ?); in other cases layers of even 1×10^{-6} cm. were found not to deviate in behavior (Sb). The atomic diameter of iron is 1.38×10^{-8} cm., and the distance between the centers of two iron atoms in the crystal lattice about 1.5×10^{-8} cm.

A layer with a thickness of 3×10^{-6} cm. is therefore built up out of 200 atoms. As a rule the author worked with layers of 5 to 6×10^{-6} cm.—i. e., 300 to 400 atoms thick. It is to be expected that, as soon as the region is reached where the constants change, these changes will be great. (For silver, for instance, n varies from 0.2 to 0.8 for thicknesses below 3×10^{-6} cm.; in the same region k varies from 5.1 to 5.6, *2*.) For this reason the author tried to ascertain with very simple apparatus whether he could find a change in the constants of iron.

To this end iron was evaporated on an oblique glass plaque, so that this was coated with a layer of iron of varying thickness (see Figure 7). The ratios between the thicknesses in given places can be calculated from the distance between these places and the glowing filament, S, and the position of the glass plaque with respect to the filament, since, considering that the dimensions of the iron bar (length 0.6 cm.) are small in comparison with the distances from the filament to the plaque (minimum distance 5.5 cm., maximum 11.4 cm.), it may be assumed that the iron comes from a "point" source. The quantity of iron precipitated per square centimeter at a place P on the glass plaque is in this case directly proportional to the sine of the angle between the line PS and the surface of the glass, and inversely proportional to the square of its distance. (The absolute thickness of the layer can be calculated on the assumption that the iron evaporates uniformly in every direction. This supposition is not quite correct, however, as the direction of the filament and the direction perpendicular to it cannot be equivalent. Presumably, all the directions perpendicular to the filament are, however, equivalent; the author's calculation was based on this supposition.)

In this way the author has calculated the ratio of the thickness of the iron at various points on the glass plaque and compared it graphically with the thickness found by the optical determination (n and k being taken to be independent of the thickness). As is shown by Figure 8, there were no systematic differences between the calculated and the meas-

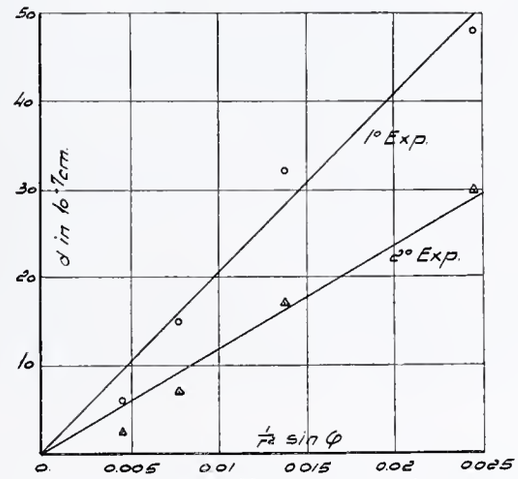

FIGURE 8. d AS A FUNCTION OF $^1/_2 r$ SIN φ

First experiment, evaporated 8.5 mg. of iron
Second experiment, evaporated 5 mg. of iron

ured ratios of thickness, from which it may be concluded that n and k are constants in this range. The thicknesses were calculated in accordance with Equation 1 (which is not an approximate one), n and k being assumed as constants.

If this supposition is correct, then there is a linear relation between the calculated thickness and $\frac{1}{r^2} \sin \varphi$, in which r is the distance from P to S and φ the angle between SP and the glass plaque.

APPLICATION TO CORROSION BY GAS OILS

The test method described here was applied to various gas oils. The fuel pump of a solid-injection Diesel engine is an instructive example of a case in which a large quantity of oil flows along places where even the slightest corrosion is inadmissible.

In order to have some basis to work on, the author calculated the order of magnitude of the corrosion permissible for a Bosch fuel pump with a plunger 6 mm. in diameter. Experience shows that such a pump no longer answers its purpose when the diameter of the plunger has worn down by about 10^{-3} cm. If this plunger has corroded over a distance of, say, 1 cm., the quantity of iron removed by corrosion is $0.6\pi \times 1 \times 10^{-3} \times 7.9 = 0.015$ gram, this being dissolved in the gas oil.

The gas oil is considered to be corrosive when the time in which this corrosion takes place is considerably shorter than the normal life of the pump (for instance, half). If, at an average load of 5 horsepower the normal life of the pump is assumed to be 30,000 horsepower-hours, then in half the time 3000 kg. of gas oil have

[1] These values for n and k cannot be correct, as is seen on closer consideration, for there is an inequality relation between n and k—viz., $\frac{4}{n}(n^2 + n^2k^2) \leq (n + 1)^2 + n^2k^2$ (*3*). Many of the values given in literature for n and k are found not to comply with the inequality relation. This has been pointed out by Veenemans (*4*).

The author is very much indebted to C. F. Veenemans of the N. V. Philips' Gloeilampenfabrieken, Eindhoven, for his valuable information on this point.

been fed through the pump. About 5 per cent of this has leaked away along the plunger, so that 150 kg. of oil have caused the wear referred to. It follows that a corrosion of only 0.1 gram of iron per ton of gas oil is important. It is clear that a gravimetric determination on a laboratory scale of the quantity of corroded iron will be very difficult, even though during the short time of flow along the plunger the gas oil may not be nearly saturated with iron, so that in a laboratory test an appreciably higher content of iron per gram of oil might be found. In the case under discussion one is thus dealing with a corrosion represented by one part of iron dissolved by ten million parts of gas oil.

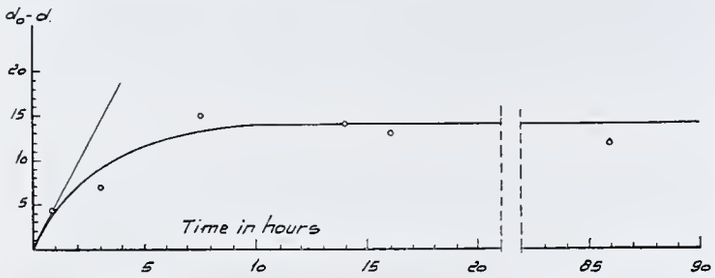

FIGURE 9. DECREASE OF THICKNESS AS A FUNCTION OF TIME OF CORROSION

To compare the various gas oils, a 15-cc. oil sample was heated with an iron plate in a test tube at 120° C. for 16 hours, after which the difference in the thickness of the plate was measured. It had been found that with a given corrosive gas oil (gas oil A) the thickness of layer removed by corrosion reaches a maximum after 16 hours. In this time the corrosive constituents in the oil have been entirely consumed, so that the corrosion after 16 hours is a gage of the total amount of corrosive constituents in 15 cc. of gas oil. (A fresh plate placed in oil that had been heated for 16 hours with an iron plate did not show corrosion.) As is always the case with corrosion phenomena, the duplicate determinations show divergences; to reduce the influence of these divergences, the author invariably placed several plates separately in a test tube with 15 cc. of liquid. For the definite determinations he used 8 plates at a time. The accuracy of the final result is then about 1.5×10^{-7} cm.—i. e., 9 atomic diameters.

Several determinations with gas oil A to find the function of time in the process of corrosion are given in Table I, and have been plotted graphically in Figure 9.

TABLE I. THICKNESS OF CORRODED LAYER AS A FUNCTION OF TIME OF ATTACK

Period of Attack	Decrease in Thickness of Iron Layer	Average
Hours	10^{-7} *cm.*	10^{-7} *cm.*
1	4–7–9–4–3–7–4	5
3	5–10–7–9–7–3–6–11	7
7.5	10–16–23–11.5	15
14	13–15.5–15	14
16	4–10–15–16–7–16–17–8	13
86	13.5–10	12

From Figure 9 and Table I it follows that the corrosion approaches a final value after about 10 hours. The final value of the thickness of layer removed by corrosion is 13×10^{-7} cm. In 15 cc. of this gas oil a maximum quantity of $13 \times 10^{-7} \times 4 \times 1$ cc. $= 52 \times 10^{-7}$ cc. $= 52.10^{-7} \times 7.8$ grams $= 4.10^{-4}$ grams of iron might therefore dissolve—i. e., 3 grams of iron per ton of gas oil. Although this quantity is relatively extremely small, it is yet 30 times as large as the 0.10 gram of iron per ton of gas oil calculated as being inadmissible. The gas oil, when flowing along the metal, therefore absorbs only a small portion—a few per cent—of the maximum soluble amount of iron. As a matter of fact, the conditions for corrosion in the fuel pump differ fundamentally from those in the laboratory test, as in the former case fresh oil is always in contact with the iron for a short time, whereas in the second case a measured quantity of oil is brought into contact with the iron for a long time. It is therefore chiefly the corrosion brought about during the first period of contact between iron and oil which is decisive for the corrosion in the pump.

As to the order of magnitude, the results obtained in practice and those in the laboratory test are found to tally very well, for if the line of contact is drawn in the origin of the corrosion curve in Figure 9 it appears that at the beginning of the process the corrosion is 5×10^{-7} cm. per hour. Assuming that a pump has an average life of 15,000 horsepower-hours when corrosive gas oil is used, the pump would have been in contact with the gas oil for about 3000 hours at a load of 5 horsepower, which would point to a wear of $3 \times 10^3 \times 5 \times 10^{-7}$ cm. $= 1.5 \times 10^{-3}$ cm. This is quite consistent with the correct order of magnitude (see above). There is, therefore, a very good agreement between the figures, considering, in the first place, that the figures of 10^{-3} cm. in the diameter to express the unserviceableness of the pump is based on an estimation, and secondly, that the temperature and the pressure of the oil in the pump differ from those in the laboratory test.

Table II shows some gas oils examined by the author arranged in the order of decreasing corrosiveness (thickness of layer measured after 16 hours' heating with an iron plaque).

TABLE II. CORROSIVENESS OF VARIOUS GAS OILS

Sample of Gas Oil	Average Decrease in Thickness of Layer[a]	Sample of Gas Oil	Average Decrease in Thickness of Layer[a]
	10^{-7} *cm.*		10^{-7} *cm.*
A	13	G	3
B	10	H	2
C	8	I	2
D	8	J	1.5
E	7	K	1
F	7	L	0
		M	0

[a] 15 cc. of gas oil after 16 hours' heating.

The results obtained here tally, in so far as it was possible to verify this, with what was known from practice about the corrosion of the gas oil samples in the fuel pump.

In Table III the acid values of some of the gas oils examined have been tabulated and compared with the maximum quantity of iron dissolved, according to the author's observations. In almost every case this quantity of iron is only a few tenths per cent or less of the amount calculated from the acid value, which shows that there is no correlation between the corrosion in the fuel pump and the acid value. It is not known what substances are responsible for the corrosion.

At a decrease in thickness of $a \times 10^{-7}$ cm., the oil has absorbed $a \times 10^{-7} \times 4 \times 7.88$ grams of iron, whereas, at an acid value b, the 15 cc. of gas oil used might have absorbed

$$b \times 15 \times \text{sp. gr.} \times \frac{\text{mol. wt. of Fe}}{2 \times \text{mol. wt. of KOH}}$$

TABLE III. LACK OF CORRELATION BETWEEN CORROSIVENESS AND ACID VALUE

Sample of Gas Oil	Decrease in Thickness of Layer	Acid Value	Iron Absorbed by corrosion	Iron Equivalent to acid value	Iron Absorbed[a]
	10^{-7} *cm.*		*Mg.*	*Mg.*	%
H	2	0.13	0.0063	0.80	0.8
F	7	1.3	0.022	8.0	0.3
L	0	4.7	0.00	29	0.00
J	1.5	2.07	0.0047	12.8	0.04
I	2	0.4	0.0063	2.5	0.3
C	8	0.14	0.025	0.86	2.9
M	0	0.25	0.000	1.55	0.00
B	10	1.75	0.032	10.8	0.3

[a] Percentage of iron absorbed with respect to the quantity of iron equivalent to the acid value.

EXAMINATION OF ALLOYS

The examination of alloys demands more caution than that of the pure metals. Small quantities of contaminations will evaporate with the rest and will be found in the layer on the glass. The author is unable to state how far the proper-

ties of the evaporated impure metal correspond with those of the solid metal, but believes that without further treatment of the metal layer they will generally differ. In fact, in many cases anticorrosive properties of an alloy are obtained by a special treatment, and, therefore, if its properties are to be studied, it is necessary to submit the test object to precisely the same treatment. Therefore it is necessary, in order to apply the method to alloys, to ascertain that the evaporated metal layer has not only the same chemical composition as the alloy to be examined, but also the same chemical properties—i. e., the test plaque has to be treated in the same manner.

The first condition—obtaining a metal layer of the same chemical composition as the alloy—may be satisfactorily fulfilled by heating the layer in a vacuum for a sufficient space of time, allowing the metals to diffuse. For instance, when evaporating brass the more volatile zinc is first evaporated and then the less volatile component copper, so that the metal layers on the plaques are white on the glass side, but red on the other. However, after heating for about 2 hours at 100° C. no difference in color was visible between the front and the back of the coating, both sides showing the color of the brass. This experiment proves that in that time interval the metal atoms have completely diffused throughout the very thin layer. To accelerate the diffusion process, the metal might be sublimed in portions, so that in the case of brass alternating layers zinc and copper would be obtained and the distance over which the diffusion has taken place would be halved. This procedure has been applied to brass and a stainless steel without experiencing any difficulties.

The possibility of also fulfilling the second condition, by giving the right treatment to the evaporated metal layer, is being studied at the moment, and the result of a preliminary experiment with a stainless steel was not unpromising. However, it is deemed expedient to defer the work until more experience has been gained.

When applying the method to other cases, each case should be regarded separately and the method should be tested as to its utility by comparison with known data.

Accuracy of the Method

The accuracy of the measurement is determined by the divergences caused by the lack of uniformity of the corrosion. After the corrosion more or less sharply outlined dark and light spots can be observed on the plaques, so that even on each individual plaque considerable divergences would be found. It is, indeed, a generally known phenomenon that in corrosion there are very great local differences, without any apparent cause. This is sometimes accounted for by assuming the existence of "nuclei," from which the corrosion is alleged to originate (in an aqueous medium these nuclei might be local elements). In this case, where the corrosion to be measured is extremely small, the local differences are relatively great. The divergences seem to be of an accidental nature, however, as appears from the observations on gas oil A. According to Gauss' law of errors

$$\frac{\sqrt{\Sigma v^2}}{\Sigma |v|} = \sqrt{\frac{\pi}{2n}} = 0.245$$

whereas $\frac{\sqrt{\Sigma v^2}}{\Sigma |v|}$ is found to be 0.23, in which v represents the difference between an observation and the average. The mean error in the average can therefore now be calculated, for it is equal to the mean deviation from the average value divided by the root of the number of observations minus 1. From this, calculations for the heavy corrosions ($>7 \times 10^{-7}$) in Table III give a mean error in the average of about 1.5×10^{-7} for eight observations. The accuracy of the observations is therefore about 1.5×10^{-7} cm. It seems to the author that this accuracy is for the present amply sufficient for a classification of products according to their corrosive properties, and for following a refining process quantitatively.

Acknowledgment

The author wishes to thank the directors of the Bataafsche Petroleum Maatschappij, The Hague, for permission to publish this article, and his collaborators, J. Voss and J. Boelhouwer, of the laboratory of the Bataafsche Petroleum Maatschappij in Amsterdam.

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Making Clean Liquid Sodium Potassium Alloy

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POTASSIUM alloys containing 25 to 50 per cent of sodium are liquid at 15° C. The liquid surface makes them very useful where the maximum reactivity of an alkaline metal is desired, especially at room temperatures. The ordinary preparation, where the elements are melted together under kerosene, gives small and dirty particles of variable composition.

The author obtained bright, shiny globules up to 2 cm. in diameter—approximately 30 grams—by the following procedure:

> A gram of the liquid alloy (made under kerosene) is transferred into 75 cc. of benzene[1] or other hydrocarbon contained in a 150-cc. beaker. A few cubic centimeters of a 10 per cent solution of ethyl alcohol (95 per cent) in benzene are slowly added until the alloy reacts sufficiently to float. With a pair of tweezers a clean piece of potassium metal is pushed into the alloy until it is assimilated. Next a piece of sodium is added, and so on until the globule is of the desired size. A convenient method of transferring the alloy is to use a small porcelain spoon that holds 3 to 4 cc. Enough solution is scooped up at the same time to keep the surface shiny.
>
> Similarly, a very dilute solution of alcohol in benzene will convert the finely divided residue from a reaction into shiny beads which may be stirred together into larger globules and recovered for future use (sometimes the addition of some potassium metal is necessary to make the liquid more mobile); or they may be slowly and safely decomposed by successive additions of a few cubic centimeters of dilute alcohol solution in benzene.

The alloy may be stored under a purified kerosene containing less than 0.5 per cent of ethyl alcohol. A hydrocarbon mixture such as the "Safety Solvent" of the Atlantic Refining Co. (boiling point range 150° to 200° C.), distilled from sodium-potassium alloy, provides a water-white nonreactive medium. The alloy is put into the kerosene in glass-stoppered bottles which are loosely closed for several hours. Then the stopper is tightened and sealed in with sealing wax. Under these conditions the alloy may be kept in a bright state for 6 months.

Received October 5, 1934.

[1] With ether solution see Midgley, T., Jr., and Henne, A. L., Ind. Eng. Chem., Anal. Ed., 1, 75 (1929).

Oxidation of Hydrazine

IX. Mono- and Di-delectronation of Hydrazine by Permanganate in Hydrochloric Acid Solution

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THE action of various oxidizing agents upon hydrazine has engaged the attention of numerous investigators, chiefly analytical chemists, whose principal motivation in the work has been the formulation of reliable nitrometric or volumetric methods for the determination of either hydrazine or some oxidizing agent.

One of the main objects of the investigations recorded in the current series of articles (*4*) has been the elucidation of the complex mechanism involved in the oxidation of hydrazine (*2*). Incidentally, in view of the circumstance that ammonia and hydronitric acid are frequently formed as products of the incomplete oxidation of hydrazine, a warning to those who would devise analytical methods involving the use of hydrazine has been sounded to the effect that "positive proof of the quantitative conversion of the hydrazine to nitrogen and water should be obtained . . . . . before reliance is placed upon any method which under ordinary conditions is subject to the error just mentioned" (*2*).

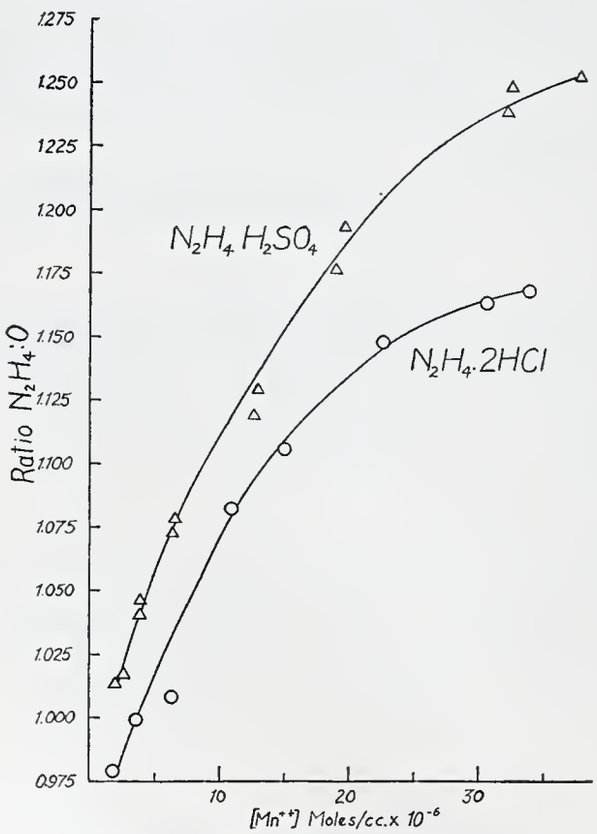

Figure 1. Influence of Manganous Ion on the Ratio of Hydrazine to Oxygen

The reaction between potassium permanganate and hydrazine sulfate in sulfuric acid solution has been studied by Petersen (*9*), Roberto and Roncali (*12*), Medri (*8*), Browne and Shetterly (*1*), Raschig (*11*), Cuy, Rosenberg, and Bray (*3*), and Purgotti (*10*), with results construed in some cases as favorable and in others as adverse to the use of this reaction in the determination of either hydrazine or permanganate. Kolthoff (*6*) characterized the Petersen method as "worthless for practical purposes," and, with the comment that "neither he (Medri) nor Browne and Shetterly succeeded in clearing up this question," suggested (*5*) the substitution of hydrochloric for sulfuric acid as a modification of the Petersen method. Kolthoff stated that the titration of a hydrochloric acid solution at boiling gave very good results, and that the oxidation corresponds quantitatively to the equation

$$N_2H_4 + 2O \longrightarrow N_2 + 2H_2O$$

Further (*6*) that "the color change may be detected sharply, and therefore hydrazine sulfate should be a good primary substance for the standardization of permanganate."

In comparing the results obtained by the Petersen-Kolthoff method in this laboratory with those obtained by the bromate method of Kurtenacker and Wagner (*7*) and by titration of hydrazine against permanganate in alkaline solution, as suggested by Sabanejeff (*13*), it was found by the authors that a given amount of hydrazine will reduce in alkaline solution nearly double the amount of permanganate reduced in hydrochloric acid solution. This is in qualitative accord with the potentiometric titrations carried out by Stelling (*14*). The results of numerous preliminary experiments indicate that one atom of oxygen, only, is required for the oxidation of one molecule of hydrazine, instead of two atoms, as stated by Kolthoff. Determinations of the ammonia in the residual solutions pointed toward the conclusion that about one-third of the nitrogen of the hydrazine is converted to ammonia, in accordance with the tentative equation

$$3N_2H_4 + 3O \longrightarrow 2N_2 + 2NH_3 + 3H_2O$$

In order to subject the reaction to careful scrutiny, an extended series of titrations has been carried out, under widely varying conditions, as well as under the particular conditions that prevailed in the work of Kolthoff.

Experimental

Materials Used. The solutions of hydrazine sulfate and hydrochloride (Kahlbaum) were standardized by the bromate method (*7*). The permanganate solutions were titrated against standard solutions of both oxalic acid and sodium thiosulfate. All burets and pipets used in the work were carefully calibrated.

Factors Studied. Among the factors found to influence the course of the reaction were (1) amount of hydrochloric acid added, (2) initial concentration of the hydrazine salt, (3) concentration of manganous ion, (4) temperature, and (5) mode of bringing the reagents together.

Procedure. The analytical procedure was in general briefly as follows: The solution obtained by adding a specified volume of 4 *N* hydrochloric acid to a measured volume of the standard hydrazine sulfate or hydrochloride solution was heated to the boiling point in a 250-cc. Erlenmeyer flask and immediately thereafter was titrated with permanganate, added drop by drop, until the pink color persisted for several minutes.

In studying the influence of the five factors enumerated above, the procedure just outlined was of necessity modified in certain cases. (1) In experiments 1 to 36 (Table I) the volume of 4 *N* hydrochloric acid was varied over a range of 5 to 40 cc. for 50 cc.

of the hydrazine solution. (2) In experiments 42 to 60 (Table II) 10 cc. of 4 N hydrochloric acid were added to different volumes of the hydrazine solution, and the total volume was made up to 52 cc. by addition of appropriate amounts of water. (3) In experiments 61 to 81 (Table III) varying amounts of manganous sulfate (0.1 N solution) were added to the hydrazine solution with 10 cc. of 4 N hydrochloric acid. (4) During the titration the temperature of the solution was permitted to fall gradually from the boiling point to about 55° C., except in experiments 4, 5, and 18, where it was maintained at 90° C. over an electric hot plate. (5) The permanganate solution was added drop by drop, with a sufficient interval between drops to permit complete discharge of the color. It was found inadvisable to introduce more than 25 cc. of the oxidant in 7 minutes, since any appreciable local excess of the permanganate favors the liberation of chlorine. The effect of a large excess of permanganate was investigated by dropping known amounts of hydrazine, both with and without hydrochloric acid, into boiling permanganate solution.

Ammonia was determined in the residual solutions by distillation from alkaline solution into a measured excess of standard hydrochloric acid.

A series of experiments was performed in order to determine the ratio of hydrazine oxidized to nitrogen evolved as gas. A water-jacketed nitrometer of the Lunge type was used. The permanganate solution was slowly dropped into the hydrazine salt solution, to which 10 cc. of 4 N hydrochloric acid had been added. The temperature of the reacting solution was maintained at 100° C. by means of a water bath, and the evolution flask was subjected to continuous mechanical agitation. Control experiments with water and permanganate solution were performed under comparable conditions in order to evaluate the correction to be applied for gases dissolved in the reagents.

Table I. Influence of Hydrochloric Acid upon Titration of Hydrazine Salt with Permanganate

Expt.	4 N HCl	$KMnO_4$ (0.08715 N)	Ratio of N_2H_4 to O	HCl (0.0514 N) Equiv. to NH_3	Ratio of N_2H_4 to NH_3
	Cc.	*Av. cc.*		*Av. cc.*	
A. Hydrazine sulfate (0.1628 gram of $N_2H_4 \cdot H_2SO_4$)					
1–3	5	27.35	1.050	16.60	1.466
4	5	27.32	1.051	16.59	1.467
5	5	27.37	1.049	...	...
6–9	8	28.78	0.997	16.30	1.493
10–14	10	29.31	0.980	15.88	1.533
15–17	20	29.89	0.961	15.30	1.603
18	20	...	...	15.25	1.608
19–21	30	29.12	0.986	15.89	1.532
22–24	40	29.77	0.964	15.51	1.569
B. Hydrazine hydrochloride (0.1322 gram of $N_2H_4 \cdot 2HCl$)					
25–28	10	29.61	0.975	15.82	1.548
29–32	20	29.96	0.965	15.51	1.578
33–36	30	29.50	0.979	15.80	1.550

In experiments 37 to 41 the nitrogen evolved by the titration of hydrazine sulfate with permanganate in hydrochloric acid solution was measured as described above. For 0.1628 gram of $N_2H_4 \cdot H_2SO_4$ the corrected volumes of nitrogen evolved were 18.38, 18.03, 18.44, 17.82, and 18.23 cc. These correspond to an average of 8.11×10^{-4} moles of nitrogen which gives an average value of 1.543 for the ratio of hydrazine to nitrogen.

Table II. Influence of Initial Concentration of Hydrazine upon Its Reaction with Permanganate in Hydrochloric Acid Solution

Expt.	N_2H_4	$KMnO_4$ (0.0900 N)	Ratio of N_2H_4 to O
	Moles $\times 10^{-4}$	*Av. cc.*	
42, 43	1.981	4.62	0.954
44, 45	3.954	9.17	0.958
46, 47	5.990	13.62	0.977
48, 49	7.964	17.82	0.993
50, 51	10.325	22.97	0.999
52, 53	11.90	26.32	1.005
54, 55	15.90	34.63	1.021
56, 57	19.87	42.62	1.036
58, 59	23.90	50.16	1.058
60	31.72	65.69	1.073

Ammonia was invariably formed as a product of the oxidation of hydrazine by permanganate under the conditions prevailing in the experiments recorded in Tables I, II, and III. In order to investigate the reaction under conditions more favorable to complete oxidation of the hydrazine to nitrogen and water, measured volumes of standard hydrazine sulfate solution mixed with either sulfuric or hydrochloric acid were introduced dropwise beneath the surface of a boiling solution of potassium permanganate prepared by dissolving 10 grams of the solid in 90 cc. of water. Boiling was continued for 10 minutes after all the hydrazine had been introduced. After the solution had cooled, the excess of permanganate was reduced by adding 10 per cent hydrogen peroxide drop by drop until the color was discharged. After the solution had been boiled to remove any excess of peroxide, it was made alkaline, and the ammonia was distilled into standard acid.

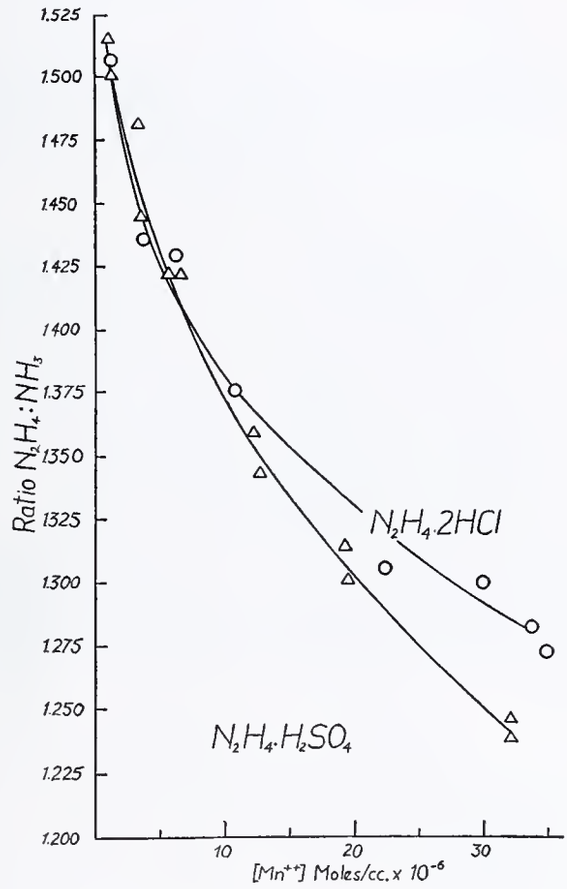

Figure 2. Influence of Manganous Ion on the Ratio of Hydrazine to Ammonia

Table III. Influence of Manganous Ion upon Reaction between Hydrazine Salt and Permanganate in Hydrochloric Acid Solution

Expt.	$[Mn^{++}]$	$KMnO_4$ (0.0900 N)	Ratio of N_2H_4 to O	HCl (0.05682 N) Equiv. to NH_3	Ratio of N_2H_4 to NH_3
	Moles/cc. $\times 10^{-6}$	*Cc.*		*Cc.*	
A. Hydrazine hydrochloride (0.1050 gram of $N_2H_4 \cdot 2HCl$)					
61	1.37	22.69	0.979	11.67	1.510
62	3.42	22.29	0.997	12.27	1.435
63	6.15	21.84	1.017	12.32	1.429
64	11.0	20.42	1.088	12.84	1.372
65	15.0	20.02	1.109	...	...
66	23.0	19.44	1.143	13.43	1.310
67	30.5	19.11	1.163	13.57	1.298
68	33.8	19.07	1.166	13.73	1.282
B. Hydrazine sulfate (0.1344 gram of $N_2H_4 \cdot H_2SO_4$)					
69	1.35	22.61	1.015	12.00	1.515
70	1.58	22.55	1.017	12.12	1.499
71	3.21	22.09	1.039	12.45	1.481
72	3.28	21.94	1.046	12.58	1.444
73	5.95	21.39	1.072	12.78	1.422
74	6.27	21.29	1.078	12.78	1.422
75	12.3	20.54	1.117	13.37	1.360
76	13.0	20.34	1.129	13.58	1.338
77	19.5	19.37	1.177	13.83	1.314
78	19.7	19.25	1.193	13.99	1.298
79	32.1	18.55	1.237	14.58	1.246
80	32.5	18.40	1.247	14.67	1.238
81	37.7	18.29	1.254	...	...

In sulfuric acid solution about 14 moles of ammonia were obtained from 19 of hydrazine. Control experiments with

weighed amounts of ammonium sulfate in place of hydrazine sulfate showed that 99 per cent of the ammonia could be recovered. In hydrochloric acid solution, however, no ammonia was obtained. Controls with ammonium chloride yielded only 10 per cent of the ammonia taken. These results show that the ammonia was oxidized by free chlorine, but not to any appreciable extent by the permanganate.

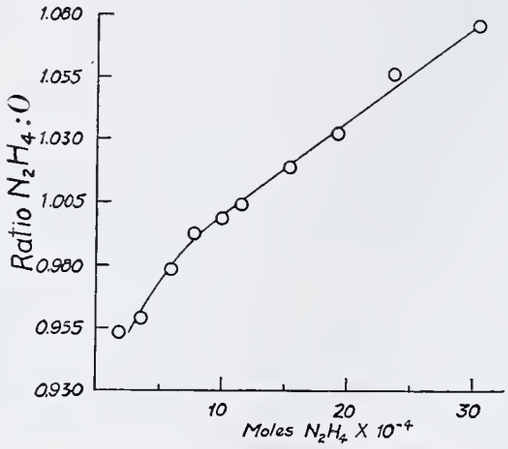

Figure 3. Influence of Hydrazine Concentration on the Ratio of Hydrazine to Oxygen

No evidence of the formation of hydronitric acid during these experiments or during the titrations was obtained from tests made under various conditions during the course of the work.

Discussion of Results

From Table I it is clear that the reaction between either hydrazine sulfate or hydrazine hydrochloride and potassium permanganate in hydrochloric acid solution does not result in complete oxidation of the hydrazine to nitrogen and water as stated by Kolthoff. Under the prevailing conditions the ratios of moles of hydrazine oxidized to (*a*) atoms of oxygen required, (*b*) moles of ammonia formed, and (*c*) moles of nitrogen liberated are in fair agreement with the equation

$$3N_2H_4 + 3O \longrightarrow 2NH_3 + 2N_2 + 3H_2O$$

which may be considered to express the resultant of two concurrent reactions of the complex delectronator (*4*) potassium permanganate: (1) complete di-delectronation of hydrazine by permanganate ion

$$N_2H_4 + 2O \longrightarrow N_2 + 2H_2O$$

and (2) incomplete mono-delectronation of hydrazine by manganic ion (3)

$$2N_2H_4 + 2Mn^{+++} \longrightarrow N_2 + 2NH_3 + 2Mn^{++} + 2H^+$$

or, in terms of oxygen used

$$2N_2H_4 + O \longrightarrow N_2 + 2NH_3 + H_2O$$

Under the conditions prevailing in experiments 1 to 41 approximately one-third of the hydrazine undergoes di-delectronation and two-thirds mono-delectronation. In experiments 6 to 9 the results approach exact conformity with this ratio. On the other hand, by increasing the concentration of manganous ion (and thereby favoring increase in concentration of manganic ion) either directly by adding 0.1 *N* manganous sulfate (Table III, Figures 1 and 2), or indirectly by increasing the concentration of hydrazine sulfate (Table II, Figure 3), the relative amount of mono-delectronation is increased, as evidenced by increase in the ratio of hydrazine to oxygen and decrease in the ratio of hydrazine to ammonia.

Values of the ratio of hydrazine to ammonia as experimentally determined agree closely with the values as calculated from the empirical equation

$$R = \frac{3}{4 - \frac{2}{R'}}$$

in which R is the ratio between moles of hydrazine and moles of ammonia, and R' the ratio between moles of hydrazine and atoms of oxygen.

Table IV. Comparison of Observed and Calculated Values of the Ratio of Moles of N_2H_4 to Moles of NH_3

Expts.	R'	R Observed	R Calculated
1–5	1.050	1.466	1.432
6–9	0.997	1.493	1.505
10–14	0.980	1.533	1.531
15–18	0.961	1.605	1.564
19–21	0.986	1.532	1.521
22–24	0.964	1.569	1.561
25–28	0.975	1.548	1.540
29–32	0.965	1.578	1.560
33–36	0.979	1.550	1.531

Values of R observed and calculated for experiments 61 to 80 are in similar accord.

In experiments 4, 5, and 18 the effect of variations in temperature upon the ratios between hydrazine and oxygen and hydrazine and ammonia was found to be negligible. In the last of these experiments, however, a liberation of chlorine began after the hydrazine had been completely oxidized, and for this reason a satisfactory end point could not be obtained.

In view chiefly of the influence of the concentration of hydrazine upon the course of its reaction with permanganate, the Petersen method as modified by Kolthoff cannot be recommended for practical use either in the determination of hydrazine or in the standardization of permanganate solutions. Under carefully controlled conditions consistent but not necessarily correct results may be obtained.

Summary

The oxidation of hydrazine by permanganate in hydrochloric acid solution has been shown to involve two concurrent reactions: (1) complete di-delectronation of hydrazine by permanganate ions

$$N_2H_4 + 2O \longrightarrow N_2 + 2H_2O$$

and (2) incomplete mono-delectronation of hydrazine by manganic ions, formed by interaction of manganous and permanganate ions

$$2N_2H_4 + O \longrightarrow N_2 + 2NH_3 + H_2O$$

The relative amount of hydrazine oxidized in these two ways depends on various factors, the influence of which has been investigated. The reaction between hydrazine sulfate and potassium permanganate in hydrochloric acid solution is therefore adjudged unsatisfactory for use either in the determination of hydrazine or in the standardization of permanganate solutions.

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Standardization of Potassium Dichromate

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The oxidation value of solid potassium dichromate or of solutions of the reagent may be determined very accurately against the primary standard, arsenious oxide, by treatment of arsenious acid in a sulfuric acid solution with less than its equivalent of dichromate, and titration of the excess reducing agent, in the presence of osmium tetroxide as catalyst and o-phenanthroline ferrous complex as indicator, either with ceric sulfate or with potassium permanganate. The titration may also be made potentiometrically with potassium bromate in a hydrochloric acid solution. Six samples of reagent quality and chemically pure potassium dichromate made by different firms showed practically 100 per cent purity.

When potassium dichromate is used as a volumetric oxidizing agent, its oxidation value is checked most satisfactorily in one of two ways. The c. p. salt may be recrystallized a number of times from water and the final product after drying used as a primary standard, or solutions of the approximate normality desired may be standardized, often by a procedure similar to that followed in an actual analysis. There are objections to both of these methods. Suitable substances of definitely known content against which to standardize a dichromate solution are not always available, and either procedure for preparing a standard solution may be time-consuming. Precise and more direct methods for testing the purity of a supply of potassium dichromate or for the standardization of solutions, preferably against primary reduction standards, are needed. There has been considerable doubt whether the salt as purchased is sufficiently pure for a primary standard. The present study shows that such standardizations may be made accurately and rapidly against arsenious oxide.

Experimental Methods and Results

Reagents and Solutions. Bureau of Standards arsenious oxide was dissolved in sodium hydroxide, and sufficient sulfuric acid added to react with the latter, followed by 10 grams of sodium bicarbonate.

The potassium dichromate was reagent quality material as received.

The ceric sulfate solutions were from large supplies made by dissolving ceric ammonium sulfate in 0.5 *M* sulfuric acid. They had been standardized against Bureau of Standards sodium oxalate (*4*).

A 0.025 *M* solution of *o*-phenanthroline ferrous complex $(C_{12}H_8N_2 \cdot H_2O)_3Fe$, was prepared by dissolving the correct amount of *o*-phenanthroline in a 0.025 *M* aqueous solution of ferrous sulfate.

The 0.01 *M* solution of the catalyst was made by dissolving 1 gram of osmium tetroxide (sometimes called perosmic acid) in 400 cc. of 0.1 *N* sulfuric acid.

Reaction between Arsenious Oxide and Potassium Dichromate. It has been stated recently by Gleu (*2*) that the titration of arsenious acid either with ceric sulfate or with potassium permanganate, using *o*-phenanthroline ferrous complex as oxidation-reduction indicator, is satisfactory at room temperature in a sulfuric acid solution, provided that a very small amount of osmium tetroxide is present as catalyst. His data are inadequate, however, to show the precision to be expected. The question arises as to whether the reaction between arsenious acid and potassium dichromate in the presence of osmium tetroxide, which appears to be a catalyst for arsenic and similar materials, would be sufficiently rapid for a direct titration. A procedure for comparing potassium dichromate against such a primary standard is of importance because the present methods of checking the normality of dichromate solutions are too indirect—such as titration with ferrous sulfate, which has been checked against permanganate standardized against Bureau of Standards sodium oxalate. This particular method, which is widely used, has been shown to be undesirable as the titration with ferrous sulfate is influenced by acidity, volume of solution, and concentration of dichromate (*1*, *3*).

In the titration of arsenious acid with potassium dichromate in a sulfuric acid solution containing two or three drops of 0.01 *M* osmium tetroxide as catalyst and two drops of 0.025 *M* *o*-phenanthroline ferrous complex as indicator, fairly concordant results could be obtained at 50° C. with solutions containing from 40 to 60 cc. of 10 *N* sulfuric acid per 100 cc. of solution at the beginning of a titration. However, as much as 0.10 cc. of 0.1 *N* dichromate in excess was ordinarily used, an indication that the reaction was too slow for a visual end point.

Table I. Potentiometric Titration of Arsenious Acid with Potassium Dichromate

(Osmium tetroxide as catalyst)

0.01 *M* OsO_4	10 *N* H_2SO_4	Normality of $K_2Cr_2O_7$
Drops	*Cc.*	
4	30	0.1003
4	40	0.1002
4	50	0.1004
4	60	0.1004
0	40	0.09985
9	40	0.1006
12	40	0.1005

The potentiometric method was tried because it permitted the use of a higher temperature with the possibility thereby of increasing the velocity of the reaction. Twenty-cubic centimeter portions of 0.1009 *N* sodium arsenite were diluted with water and the volume of 10 *N* sulfuric acid specified in Table I to 100 cc. A few drops of 0.01 *M* osmium tetroxide were added and the arsenic was titrated potentiometrically at 70° to 80° C. with 0.1004 *N* potassium dichromate. The results obtained are shown in Table I. The reaction is quantitative, but the titration much too slow to be of any practical value. With no catalyst too much of the dichro-

Table II. Titration of Excess Arsenite with Ceric Sulfate
(Osmium tetroxide as catalyst and *o*-phenanthraline ferrous complex as indicator)

0.09940 *N* Na_3AsO_3	5 *N* H_2SO_4	0.09976 *N* $K_2Cr_2O_7$	Vol. at Beginning of Titration	0.08 *N* $Ce(SO_4)_2$	Normality of $K_2Cr_2O_7$	Remarks
Cc.	*Cc.*	*Cc.*	*Cc.*	*Cc.*		
25	10	0	100	30.85 } 30.86 }		Standardizations
25	10	20	100	6.12	0.09960	
25	30	20	100	6.12	0.09960	
25	50	20	100	6.11	0.09965	End point not as sharp
25	10	15	100	12.28	0.09973	
25	10	10	100	18.50	0.09950	
25	40	20	400	6.12	0.09960	Soln. stood 5 min. after adding $K_2Cr_2O_7$
10	10	5	100	6.14	0.09980	
50	15	45	150	5.93	0.09982	
50	15	40	150	12.18	0.09973	
50	40	40	400	12.18	0.09973	
25[a]	0	20	100	6.11	0.09965	End point not as sharp
25[b]	0	20	100	6.12	0.09960	End point not as sharp
25[b]	10	20	100	6.12	0.09960	End point not as sharp
		0.09853 *N*				
25	10	25	100	0.80	0.09682	
25	10	25	100	0.37	0.09821	Soln. stood 5 min. after adding $K_2Cr_2O_7$
25	10	25	100	0.34	0 09833	Soln. stood 10 min. after adding $K_2Cr_2O_7$
25[c]	10	20	100	6.43	0.09836	Reaction a little slow
25[d]	10	20	100	6.43	0.09836	Reaction a little slow
25[e]	10	20	100	6.46	0.09826	Had to titrate at 50° C.
		0.05036 *N*				
15	10	20	100	6.06	0.05015	Soln. stood 5 min. after adding $K_2Cr_2O_7$
30	10	50	100	5.82	0.05026	Soln. stood 5 min. after adding $K_2Cr_2O_7$
0.02510 *N*		0.02564 *N*		0.027 *N*		
25	10	0	100	23.30 } 23.31 }		Standardizations
15	10	10	100	4.57	0.02535	Soln. stood 5 min. after adding $K_2Cr_2O_7$
50	10	40	100	8.53	0.02563	Soln. stood 5 min. after adding $K_2Cr_2O_7$

[a] 10 cc. of 70 per cent $HClO_4$ present.
[b] 5 cc. of HNO_3, sp. gr. 1.42, present.
[c,d,e] 10, 15, and 25 cc. of 2 *M* KCl added before $K_2Cr_2O_7$. Four drops of OsO_4 used.

mate solution was used, doubtless because of the slowness of the reaction, and even with 9 or 12 drops of the osmium tetroxide the reaction seemed only slightly more rapid.

Since the reaction between arsenious acid and potassium dichromate is too slow to permit of direct titration, a procedure involving treatment of the former in sulfuric acid solution with less than its equivalent of dichromate, and back-titration of the excess arsenious acid with ceric sulfate in the presence of osmium tetroxide as catalyst and *o*-phenanthroline ferrous complex as indicator was investigated. In the experiments listed in Table II, the measured volume of sodium arsenite was treated with sulfuric acid and sufficient water so that after the addition of the dichromate the volume of the solution was that recorded. Three drops of 0.01 *M* osmium tetroxide and two drops of 0.025 *M* *o*-phenanthroline ferrous complex were added, and the titration was made with ceric sulfate. Four different dichromate solutions were used. In the third column is recorded the normality of each of these solutions on the basis of 100 per cent purity and in the last column the experimental values obtained.

This method of standardizing dichromate solutions is quantitative over a wide range in experimental conditions. If the excess of arsenious acid is very small a few minutes should be allowed for the reaction to be complete. It is immaterial whether the indicator is added before the dichromate or just before the titration with ceric sulfate, but the osmium tetroxide must not be added before the dichromate. The data in Table II indicate also the possible concentration of chloride ion for satisfactory results.

To check this method more closely, four sets of experiments were made to obtain the purity of the potassium dichromate in terms of its oxidation value. In one series, samples of arsenious oxide, of slightly more than 1 gram, were treated in a 600-cc. beaker with a little water and 1 gram of sodium hydroxide, and the mixture was warmed until solution was complete. Water and 50 cc. of 5 *N* sulfuric acid were added. Then 1 gram or slightly less of potassium dichromate, dried at 100° to 110° C. for 4 hours, was added, the solution stirred, diluted to 400 cc., and allowed to stand for 5 minutes. Three drops each of 0.025 *M* *o*-phenanthroline ferrous complex and of 0.01 *M* osmium tetroxide were added and the arsenious acid was titrated with 0.025 *N* ceric sulfate. Because of the dark green color of the chromic salt, the volume of the solution should be 400 to 500 cc. If the beaker is placed on a piece of white paper, the operator in looking down through the solution will observe a rose tint in the green liquid. When near the end point, this rose color becomes more pale. At the end point it disappears and the solution changes to a clear green in color. In the experiments listed in Table III, the excess of arsenite was such as to require as little as 8.40 cc. of the 0.025 *N* ceric sulfate in one case, and as much as 43.33 cc. in another case.

In the second series, the procedure was the same as in the first, except that 0.044 *N* potassium permanganate was used to titrate the excess of arsenious acid.

In the third series, the samples of arsenious oxide were placed in 400-cc. beakers and dissolved in the usual way, the solution was treated with 10 cc. of hydrochloric acid (sp. gr. 1.18), and diluted with water to 100 cc. Potassium dichromate samples of a little less than 1 gram were added, the solution was stirred and allowed to stand a few minutes before potentiometric titration with 0.025 *N* potassium bromate. The strength of the bromate solution was checked potentiometrically against 0.025 *N* sodium arsenite in a hydrochloric acid solution.

In the fourth series, the procedure was the same as in the first, except that the dichromate had been fused in an electric furnace, and after being broken up into small crystals had been dried for 4 hours at 100° to 110° C.

Table III. Oxidation Value of Reagent Quality Potassium Dichromate

Agent for Titrating Excess H_3AsO_3	Oxidation Value of $K_2Cr_2O_7$
0.025 *N* $Ce(SO_4)_2$ in H_2SO_4 soln.	100.01, 100.01, 100.00, 100.01
0.044 *N* $KMnO_4$ in H_2SO_4 soln.	100.05, 100.02, 99.99, 100.00
0.025 *N* $KBrO_3$ in HCl soln.	100.03, 100.05, 100.01, 100.01
0.025 *N* $Ce(SO_4)_2$ in H_2SO_4 soln. (fused $K_2Cr_2O_7$ used)	99.99, 99.98, 100.00, 99.99

Tests made on samples of potassium dichromate from a number of chemical houses are listed in Table IV. The samples were fused, and then broken up and dried for 4 hours at 100° to 110° C. Dilute ceric sulfate was used in determining the excess of arsenious acid.

Table IV. Oxidation Value of Samples of Potassium Dichromate after Fusion

Material	Oxidation Value
Baker Analyzed	99.98, 100 00, 99.92
Baker and Adamson, reagent	99.99, 100.03, 100.02
Coleman and Bell, c. p.	100.02, 100.02, 99.96
Mallinckrodt, a. r.	100.00, 99.96, 100.04
Merck, c. p.	99.95, 100.02, 100.00
Manufacturer not stated, reagent	99.94, 99.94, 99.90

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(1) Eppley and Vosburgh, *J. Am. Chem. Soc.*, 44, 2148 (1922).
(2) Gleu, *Z. anal. Chem.*, 95, 305 (1933).
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Estimation of Unsaturation in Aliphatic Hydrocarbons by Bromide-Bromate Titration

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It is well known that there is no generally applicable method for the estimation of unsaturation in hydrocarbons. Among those proposed, the bromide-bromate titration is one of the best and most simple. Substitution is therein reduced to a minimum, since bromine is liberated only slowly from an acidified, standardized solution of potassium bromide and bromate. Francis (*3*) has modified the original form of this procedure and applied it to the estimation of unsaturation in petroleum. Cortese (*1*) has titrated a number of pure liquid hydrocarbons in this way and Davis (*2*) has used it in determining unsaturation in gases. Occasional references occur elsewhere.

Because of its obvious utility in the identification of hydrocarbons, the authors have attempted to determine more precisely the limits of its applicability.

Experimental

The preparation and standardization of the solutions are described by Francis (*3*). His method of titration was modified slightly, as follows:

The calculated amount[1] of standardized bromide-bromate solution was run into a 118-cc. (4-oz.) glass-stoppered bottle, 0.5 cc. of hydrocarbon was then added, and finally 15 cc. of 10 per cent sulfuric acid. The bottle was stoppered quickly and shaken well, until the bromine color vanished and did not reappear when agitation was temporarily stopped. If, instead of disappearing, a visible bromine color still remained after 2 minutes of shaking, 5 cc. of 15 per cent potassium iodide were added and the liberated iodine was titrated with 0.2 *N* thiosulfate solution. If, on the other hand, the bromine color disappeared, more bromide-bromate solution was added, 1 cc. at a time, until a visible yellow color finally persisted after 2 minutes of shaking. Titration was then completed as described.

In Table I, the results are recorded as bromide-bromate numbers and as the number of double bonds found. The former is the number of centigrams of bromine absorbed by 1 gram of hydrocarbon, and is so designated in order to emphasize the method of determination.

Table I. Bromide-Bromate Titration Values of Hydrocarbons

Compound	Bromine-Bromate Number		Number of Double Bonds	
	Found	*Calculated*	*Found*	*Present*
Alkenes[a]				
1-Hexene	192	190	1.0	1
1-Heptene	157, 155	163	1.0	1
2-Heptene	182	163	1.1	1
3-Heptene	162, 161	163	1.0	1
5-Metbyl-1-hexene	164	163	1.0	1
4,4-Dimethyl-1-pentene	177	163	1.1	1
2-Octene	127	143	0.9	1
1-Nonene	126, 129	127	1.0	1
4-Nonene	126, 125	127	1.0	1
4-Methyl-2-octene	127, 125	127	1.0	1
4,6-Dimethyl-2-heptene	133, 133	127	1.0	1
1-Decene	116, 116	114	1.0	1
1-Hexadecene	70.5, 70.3	71.3	1.0	1
Cycloalkenes[a]				
Cyclohexene	193, 192	195	1.0	1
1-Methyl-1-cyclohexene	158, 159	167	1.0	1
1-Cyclohexyl-2-propene	125, 125	129	1.0	1
4-Cyclohexyl-2-pentene	112	105	1.1	1
4-Cyclohexyl-2-heptene	83	89	0.9	1
Alkadienes[a]				
1,3-Pentadiene	470	471	2.0	2
2,3-Dimethyl-1,3-butadiene	385	390	2.0	2
2,4-Heptadiene	325, 326	333	2.0	2
2,4-Octadiene	281, 277	291	1.9	2
4-Methyl-1,5-heptadiene	244, 247	291	1.7	2
2,2-Dimethyl-3,4-bexadiene	294, 285	291	2.0	2
4,5-Dimethyl-2,6-octadiene	193	232	1.7	2
4-Propyl-1,5-beptadiene	178, 183	232	1.6	2
4-Allyl-2-octene	170	210	1.6	2
4,5-Dipropyl-2,6-octadiene	146	165	1.8	2
4,5-Dibutyl-2,6-octadiene	125	144	1.7	2
Terpenes[b]				
Carvene	246	235	2.1	2
d-α-Pinene	243, 248	118	2.1	1
l-α-Pinene	171, 170	118	1.4	1
l-β-Pinene	256	118	2.2	1
Phellandrene	175	235	1.5	2
d-Phellandrene	198	235	1.7	2
l-Phellandrene	155	235	1.3	2
Sabinene	250	118	2.1	1
Cedrene	121	78	1.6	1
Caryophyllene	134, 143	157	1.8	2
	64.8, 63.4		0.8	
Alkines[a]				
2-Heptine	122	333	0.7	2
3-Heptine	234, 230	333	1.4	2
1-Octine	142	291	1.0	2
2-Octine	163, 156	291	1.1	2
4-Nonine	106	258	0.8	2
1-Hexadecine	31	144	0.4	2

[a] Synthetic, excepting cyclohexene and 1-methyl-1-cyclohexene from Eastman. The preparation of tbese compounds was aided by a generous grant to S. P. Mulliken from tbe Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

[b] The majority of these terpenes were kindly contributed by Schimmel and Co., Miltitz near Leipzig, through the courtesy of F. E. Watermeyer, president of Fritzsche Bros., their American representatives. Tbe remainder were from various sources. Tbese compounds were not redistilled. Different values for tbe same compound indicate samples from two different sources.

Summary

The bromide-bromate titration can be used with a fair degree of accuracy for the titration of most alkenes and also to determine the number of double bonds present in cycloalkenes and in alkadienes, although less accurately for their quantitative estimation. Its application under ordinary conditions, in the presence of atmospheric oxygen, to alkines and to cycloalkadienes, such as terpenes, is of doubtful value. This confirms the results obtained by Cortese (*1*).

Literature Cited

(1) Cortese, *Rec. trav. chim.*, 48, 564 (1929).
(2) Davis, Crandall, and Higbee, Ind. Eng. Chem., Anal. Ed., 3, 108 (1931).
(3) Francis, Ind. Eng. Chem., 18, 821 (1926).

[1] To the observed boiling point of the hydrocarbon 25° were added. Tbe amount of bromide-bromate solution theoretically necessary to titrate an alkene of the boiling point tbus found was calculated and used, after subtraction of 2 c. Hence, less tban the amount theoretically necessary for the hydrocarbon at band was always used at the beginning.

Received November 1, 1934. Abstract of a portion of a dissertation submitted by R. L. Wakeman of the faculty of the Massacbusetts Institute of Tecbnology in partial fulfilment of the requirements for the degree of Doctor of Philosopby, June, 1930. Contribution No. 114 from the Researcb Laboratory of Organic Chemistry, Massachusetts Institute of Tecbnology.

A New Laboratory Machine for Evaluating Breakdown Characteristics of Rubber Compounds

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A new laboratory flexometer for evaluating breakdown and blowout characteristics of rubber compounds is described. This machine differs from previous machines in that the flexing forces are measured at all times, and initial failure of the sample is accurately indicated before complete blowout occurs. The test specimen used, 3.81 cm. in diameter and 3.81 cm. in length, is rotated between two parallel plates, the base being off-center referred to the top. Stocks may be compared under conditions of "constant load" or "constant deflection."

By means of this machine it has been found that the flexing force does not decrease as the sample is flexed, but actually increases, indicating that a marked structural change has taken place in the rubber. The effects on breakdown characteristics due to changes in volume loading, type of pigment, and other compounding variations are shown. Tests on commercial stocks show good correlation with road tests on tire and carcass compounds.

With the advent of modern high-speed mechanical equipment manufactured by the automotive, railway, electrical, and other industries, there has resulted an increase in the use of rubber compounds for absorbing vibration and eliminating shock and noise. Quick acceleration, high speeds, rapid application of brakes, and heavy live loads, in both mobile and stationary equipment, have imposed severe distortional and destructive stresses on rubber parts. The heat generated in many of these parts, such as solid tires, carcass stocks, and various mechanical goods, is sufficient to produce decomposition of the rubber compound, resulting in actual blowout. In other instances the stocks take on an excessive permanent set which causes severe misalignment of parts. The compounder has found it necessary to use all the skill and ingenuity at his command to cope with these conditions. Zinc oxides are used in large percentages in many of these compounds and it has been found that various zinc oxides give different performance results.

To develop zinc oxides and rubber compounds which will better withstand the more severe conditions, a flexing machine is of considerable value. To be of utmost value this machine must simulate service conditions, permit the evaluation of all the forces producing flexure, and accurately indicate the end point, or initial failure, of the test specimen.

A study of several existing flexing machines (*1*, *2*, *4*) disclosed that they do not completely fulfill the above conditions. On none of these machines is it possible to measure all the flexing forces, and the end point or initial failure of the test specimen is not indicated. Attempts to measure the power required to break down the specimen by means of wattmeters or other power-measuring devices have been defeated because of the low mechanical efficiency of the apparatus.

Since none of the above machines fulfilled all the requirements, the authors' technical organization undertook the design and construction of a machine incorporating the desirable features. It was believed that the flexing forces could be more conveniently measured if the test specimen were rotated. A cylindrical test specimen rotating at 875 r. p. m. is used.

Description of Machine

Figure 1, a drawing of the complete machine, shows the mechanism for loading and flexing the test specimen, as well as the means by which the flexure and flexing forces are measured.

Test specimen 1 is accurately positioned between face plates 2 and 3 through use of centering jig 4. By release of jack 5, the load is applied vertically to the test specimen from weights 6, acting through lever arm 7, which rests on top of vertical shaft 8, producing compression in the test specimen. This shaft is driven by pulley 9 which is belted to a vertical shaft motor. The lower face plate, 3, rests on vertical shaft 10 and is driven by the upper shaft and face through the test specimen which acts as a coupling. Vertical shaft 10 and carriage 11 are mounted on rollers 12 that ride on track 13.

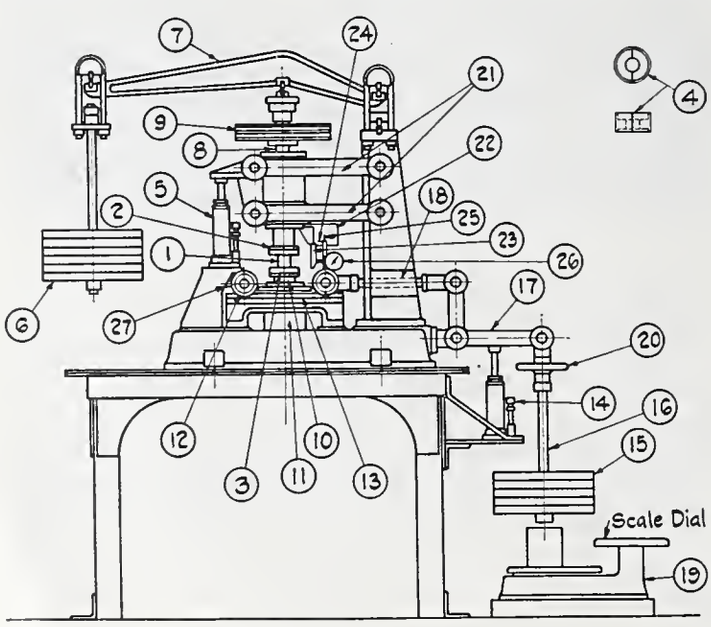

Figure 1. Diagram of Machine

1. Rubber test specimen
2. Upper face plate
3. Lower face plate
4. Centering jig
5. Hydraulic jack
6. Vertical load weights
7. Lever
8. Upper vertical shaft
9. V-belt pulley
10. Lower vertical shaft
11. Carriage
12. Carriage rollers
13. Track
14. Hydraulic jack
15. Horizontal load weights
16. Hanger for weights
17. Bell crank
18. Link
19. Platform scale
20. Handwheel for deflection adjustment
21. Parallel linkage
22. Double divided scale
23. Straight edge for micrometer
24. Pointer for vertical compression
25. Pointer for horizontal deflection
26. Dial-type micrometer gage
27. Carriage stop

In addition to the vertical compression, horizontal deflection is produced in the test specimen by release of jack 14 which allows weights 15, acting through hanger 16, bell crank 17, and link 18, to move carriage with face plate 3 horizontally to the right along track 13. Weights 15 rest on platform of scale 19 during the progress of the test. Changes in the horizontal deflecting force and the initial failure are indicated by this scale. This platform scale is used in all tests except the stepped-increase horizontal load test, when it is removed and suitable dead weights are added to hanger 16 at chosen intervals. Changes in horizontal deflection are made by adjusting handwheel 20 which changes the length of hanger 16. Upper shaft 8 is maintained vertically by parallel linkages 21 and the axes of upper and lower shaft are parallel throughout the test.

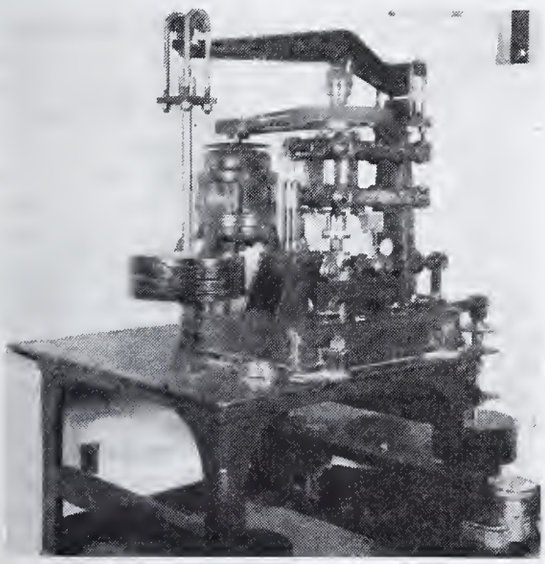

FIGURE 2. COMPLETE MACHINE

Drive and all mechanism for loading and flexing the specimen, also devices for measuring the flexure and flexing forces.

From a study of Figure 1 it is evident that the vertical load may be varied to suit different conditions of testing by changing weight 6, and that changes in horizontal deflection and horizontal load may be made by suitable adjustment of handwheel 20. The design permits modifications whereby the vertical or horizontal load, or both, may be held constant, resulting in variable deflections, or the deflections may be held constant, resulting in variable loads.

Changes in vertical compression and horizontal deflection of the test specimen may be observed throughout the test by means of double divided scale 22, straight edge 23, pointers 24 and 25, and dial-type micrometer gage 26. Scale 22 and straight edge 23 are attached to the upper assembly, while pointers 24 and 25 and micrometer gage 26 are attached to the lower assembly. Pointer 24 indicates the vertical compression of the specimen on horizontal graduations of scale 22, while pointer 25 indicates the horizontal deflections on vertical graduations of scale 22. The horizontal deflection may be more accurately measured by using straight edge 23 and dial-type micrometer gage 26 which is readable to 0.00127 cm. (0.0005 inch).

Jack 14 is used to return the lower face plate 3 with carriage 11 to concentric alignment with upper face plate 2. Stop 27 prevents over-travel of the carriage. Jack 5 raises the upper assembly for the removal or insertion of test specimens.

Figure 2 is a photograph of the complete machine. Figure 3 is a close-up of the machine, showing the test specimen running under vertical compression and horizontal deflection.

Plates 2 and 3 are faced with a Bakelite Micarta compound, chosen to obtain a balance between the applied mechanical loads and the thermal retention which would most nearly simulate the usual service conditions. An asbestos fabric compound was chosen for its ability to stand up under high temperature without deterioration. Figure 4 gives the effects of two different Micarta compounds when identical specimens were used. Compound 256 deteriorated rapidly and was discarded in favor of No. 200.

TEST SPECIMENS

The specimens (Figure 5, *A*) used in all the tests recorded in this paper were 3.81 cm. (1.5 inch) in diameter and 3.81 cm. (1.5 inch) high and cured in the laboratory in an eight-cavity mold. Specimens of other sizes and shapes may be cut from cured articles. For comparison, the size and shape of the specimens in any series of tests must be identical and circular symmetrical specimens are preferable. The uncured stock is sheeted out on a 15.2 × 30.5 cm. (6 × 12 inch) laboratory mill to about 0.381 cm. (0.15 inch) in thickness. Strips 5.72 cm. (2.25 inch) wide, with a length equal to the width of the sheeted stock, are cut off and rolled up with the grain of the rubber parallel to the axis of the cylinder. As in tensile testing, grain direction markedly affects the results, in some instances causing variations of 50 to 100 per cent, making it necessary to have the grain always in the same direction.

TESTING PROCEDURE

Testing under high vertical loads and high horizontal deflections sets up disruptive forces in the specimens which result in early breakdown and unsatisfactory data. Some specimens failed in 2 minutes when excessive vertical loads and horizontal deflections were applied. Tests conducted for a duration of 30 to 60 minutes are desirable.

The type of test determines the procedure, which generally consists in adjusting the machine for proper loads and deflections, and taking and recording readings of vertical compression (*VC*), horizontal deflection (*HD*), and horizontal load (*HL*) at appropriate intervals, usually 2 to 5 minutes until failure occurs.

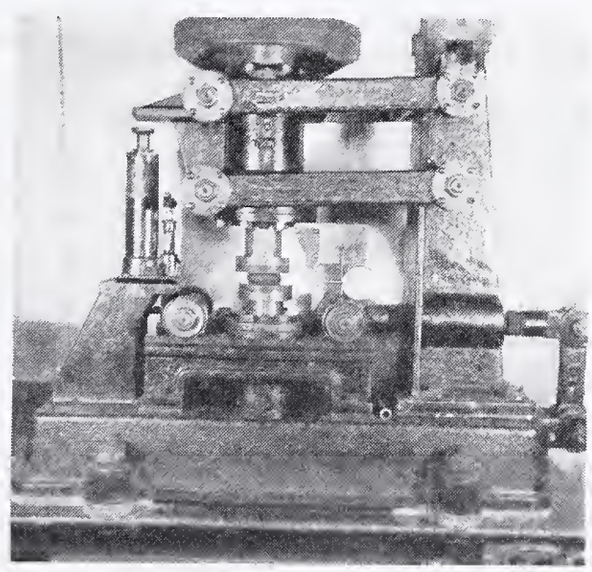

FIGURE 3. CLOSE-UP OF MACHINE WITH THE SPECIMEN RUNNING UNDER LOAD AND DEFLECTION

Gages and scales for determining vertical compression and horizontal deflection are clearly shown.

The temperature of the face plates (2 and 3, Figure 1) at start of the test has a marked effect on the results. Before any tests are conducted, a dummy specimen is run in the usual way to bring the plates to operating temperature. Tests are started with a face plate temperature of 57.2° to 62.8° C. (135° to 145° F.). The temperature is measured by a copper-constantan thermocouple at the start of each test. During the test the temperature of the specimen may be taken at failure, or any intermediate point, by stopping the machine and inserting a modified hypodermic thermocouple into the center of the specimen.

The machine is readily adapted to a wide variety of testing conditions:

Constant Horizontal Deflection. Constant vertical load resulting in variable compression; constant vertical compression resulting in variable load; variable horizontal load; and measurement of flexure set.

Constant Horizontal Load. Constant vertical load resulting in variable compression; constant vertical compression resulting in variable load; variable horizontal deflection—stepped increase horizontal load and matched horizontal load—and measurement of flexure set.

For flexure set test, specimens are removed from the machine before initial failure and the percentage decrease in thickness is determined.

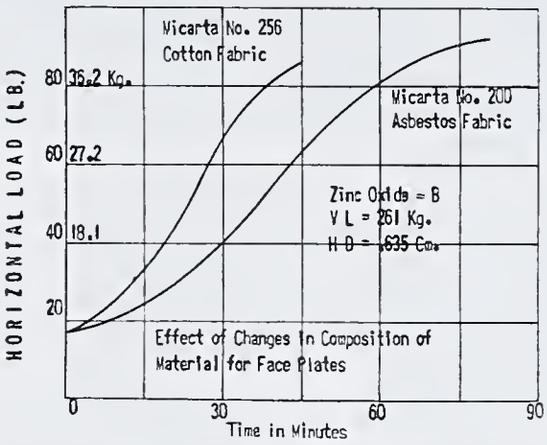

Figure 4. Constant Horizontal Deflection Test with Micarta Plates

Constant Horizontal Deflection Tests. In this method of testing, the desired horizontal deflection is set by means of handwheel 20 (Figure 1), and no further adjustments in this deflection are made in any series of comparable tests.

The test specimen is centered in the machine by means of jig 4. Vertical load weights 6, acting on upper plate 2, are allowed to compress the specimen by release of jack 5. After the machine is started, rotating face 3 is pulled off-center (horizontally deflected) from rotating face 2 by release of jack 14. Readings of vertical compression, horizontal deflection, and horizontal load are taken at regular intervals and properly recorded.

As upper face plate 2 and assembly drop down during the progress of the test they also move to the right, as parallel linkages 21 describe an arc in the downward travel. Also with an increase in horizontal load, weights 15 resting on platform of scale 19 rise, because of a lessening of the load on the scale which causes lower face plate 3 and carriage to move to the left. The effect of these movements is to decrease slightly the horizontal deflection applied to the test specimen. This condition might be interpreted as creating a considerable source of error, but when similar stocks are compared the net differences in horizontal deflections at comparable periods are extremely small. If it is desirable to maintain this deflection constant throughout the test, this is accomplished by frequent adjustment of handwheel 20 and reference to the dial-type micrometer gage. Table I and Figure 6 show these differences.

Table I. Constant Horizontal Deflection Tests

Breakdown data on zinc oxides A, B, and C
VL, 261 kg. *HD*, 0.714 cm.

	Oxide	Time	Vertical Compression	Horizontal Deflection	Horizontal Load
		Min.	*Cm.*	*Cm.*	*Kg.*
Start of test	A	0	0.970	0.690	15.2
	B	0	0.960	0.696	14.5
	C	0	0.940	0.691	16.2
Half breakdown	A	13.2	1.245	0.671	23.8
	B	21.7	1.316	0.668	24.7
	C	28.5	1.316	0.660	26.5
Breakdown	A	26.4	1.910	0.630	33.3
	B	43.4	1.958	0.625	36.5
	C	57.0	1.930	0.620	34.0

During these tests the horizontal load necessary to deflect the specimen increases in value until initial failure (Figure 5, *E*), which is indicated by a sudden decrease in the load (Figure 7) or, in exceptional cases, by a failure of the load to increase. If a test is continued beyond this point the load further decreases until blowout of the specimen, which may occur within a few seconds or many minutes.

Experience has indicated that tests carried to complete destruction are not indicative of the service life of a rubber compound. Since the point of initial failure can be accurately determined, the authors' tests are not run to complete destruction or blowout. Figure 7 shows constant horizontal deflection test data on two identical specimens run to complete blowout. Correlation is good as regards initial failure and poor as regards blowout.

The increase in horizontal load occurs with an increase in vertical compression, or flattening, of the specimen which was at first thought to cause the increase in load. Tests (Figure 16) conducted with a constant vertical compression and constant horizontal deflection show that the horizontal load increased as before and was not due to the change in shape of the test specimen. The increase in horizontal load is probably due to a continuous change in permanent set as well as to an increasing stiffness and change in the properties of the rubber compound as the temperature of the specimen increases. A study of the rotating specimen with the stroboscope reveals very little torsion. It was thought that this might affect the horizontal load, but even excessive torsion produced by braking the lower face plate until slippage occurred had little or no effect.

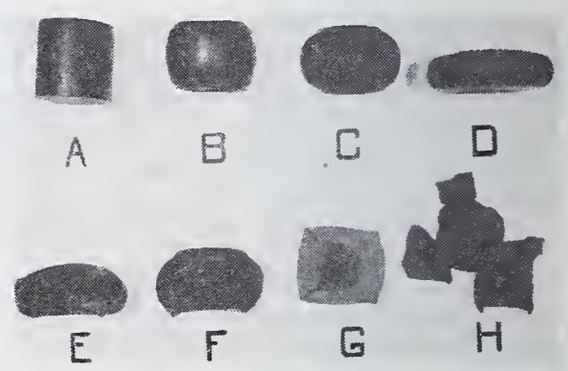

Figure 5. Representative Types of Breakdown Produced by New Machine

A. Original rubber test specimen
B. First degree of permanent set; specimen removed from machine at about one-third breakdown time
C. Second degree of permanent set; specimen removed from machine at about one-half breakdown time
D. Third degree of permanent set on undercured stock
E. Initial failure, showing the porous center which is the first indication of breakdown, as shown by a decrease in horizontal load. Typical of high-zinc stocks
F. Breakdown, split type; generally follows type *E*. Typical of high-zinc stocks
G. Sticky decomposed center type, characteristic of gas-black stocks, such as pneumatic tire treads
H. Mechanical breakdown or blowout due to excessive vertical load and horizontal deflection

An autographic attachment is being designed which will automatically record the vertical compression and horizontal load and stop the machine when initial failure occurs. Other changes are also contemplated which will practically eliminate the variation in horizontal deflection.

Constant Horizontal Load Tests. If the platform scale be removed and a dead weight sufficient to produce failure be used for horizontal loading, the specimen is pulled out of the machine because of excessive horizontal deflection. If, then, a dead weight be used which can be sustained by the specimen at the start of the test, a progressive stiffening of the stock takes place during test which actually lifts the dead weights and results in decrease of the horizontal de-

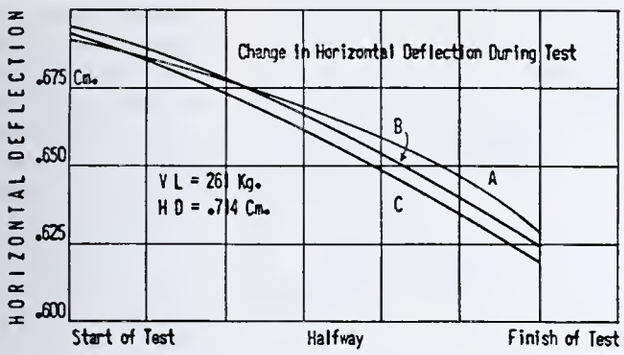

FIGURE 6. CONSTANT HORIZONTAL DEFLECTION TEST

Zinc oxides A, B, and C

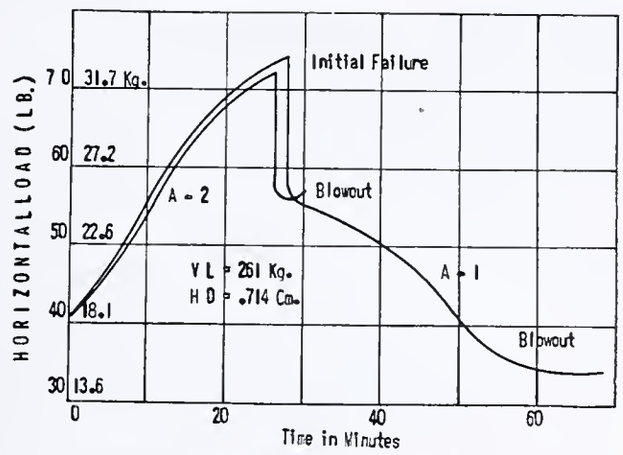

FIGURE 7. CONSTANT HORIZONTAL DEFLECTION TEST

Zinc oxide A

flection to a point where no failure is possible even under prolonged testing.

Since failure is not possible under the conditions outlined above, tests are conducted with a stepped increase in the horizontal load. Platform scale 19 is removed from the machine and weights 15 are allowed to hang free during the test. These weights are adjusted to the maximum that the specimen will sustain at the start of the test. At regular time intervals the weight is increased by certain increments until failure occurs. In this test the stocks are compared under identical loading conditions and the horizontal deflection is dependent on the modulus, stiffness, etc., of the rubber compound. (For stepped increase horizontal load test data see Figures 17 and 29 and Table III.)

An alternate method of comparing two or more stocks under the same loading conditions is to run them under the constant horizontal deflection test conditions as outlined above and then retest, matching the horizontal load-time curves one to the other by continuous adjustment of handwheel 20, Figure 1. This is known as the matched horizontal load test.

RESULTS OF TESTS. The value and scope of the machine are demonstrated by tests conducted on stocks containing various zinc oxides, and on commercial stocks furnished by several rubber companies. The effect of cure and variations in compounding, such as particle size of zinc oxide and volume loading, is shown. The effect of changes in vertical load, vertical compression, horizontal load, and horizontal deflection is also shown.

Fine, medium, or coarse zinc oxides were used in all the specimens tested and were compounded with the rubber according to the formula given in Table II, the only exceptions being the commercial stocks furnished by the manufacturers. Photomicrographs of these zinc oxides are shown in Figure 8. These oxides are made by the electrothermic process and are of the same chemical purity. Figures 9, 10, 11, and 12 give the usual physical test data on these rubber compounds and show correlation of hardness, tensile, and abrasion with particle size.

TABLE II. FORMULA FOR HIGH-ZINC STOCKS

Rubber	100.0
Sulfur	4.0
Di-*o*-tolylguanidine	1.4
Zinc oxide	150.0
Gas black	9.0

All specimens cured 65 minutes at 286° F. (141.1° C.).

BREAKDOWN TEST DATA

CONSTANT HORIZONTAL DEFLECTION TEST. Figures 13, 14, and 15 and Table I show breakdown test data on stocks containing the various oxides. A 261-kg. (575-lb.) constant vertical load and a 0.714-cm. (0.281-inch) horizontal deflection were applied to the specimen during these tests.

TABLE III. STEPPED INCREASE HORIZONTAL LOAD TESTS

Breakdown data on zinc oxides A, B, and C
Vertical load = 261 kg.

	Oxide	Time	Vertical Compression	Horizontal Deflection	Horizontal Load[a]
		Min.	*Cm.*	*Cm.*	*Kg.*
Start of test	A	0	0.930	0.676	17.0
	B	0	1.113	1.461	17.0
	C	0	1.016	1.067	17.0
Half breakdown	A	11.8	1.034	0.663	23.1
	B	12.0	1.481	0.605	23.1
	C	9.6	1.113	0.630	17.0
Breakdown	A	23.5	1.387	0.737	35.4
	B	24.0	1.626	0.663	35.4
	C	19.2	1.288	0.813	29.3

	Min.	*Kg.*
[a] Horizontal load	0–10.0	17.0
	10.5–15.0	23.1
	15.5–20.0	29.3
	20.5–25.0	35.4

A B C

FIGURE 8. PHOTOMICROGRAPHS (× 1500) OF ZINC OXIDES

d_3, diameter in microns of particle of average surface (S)
S, specific surface in square meters per gram

ZnO A	ZnO B	ZnO C
d_3 0.42	d_3 0.65	d_3 0.93
S 2.59	S 1.70	S 1.20

Figure 13 shows the horizontal loads, or deflecting forces, on the specimens plotted against time of test in minutes. These tests were stopped at initial failure and not carried to blowout, as shown on Figure 7. The horizontal load, or flexing force, increases at different rates for the various stocks and indicates a marked stiffening of the compounds. This flexing force could not be measured on any of the previous machines.

Figure 14 shows the progressive increase in vertical com-

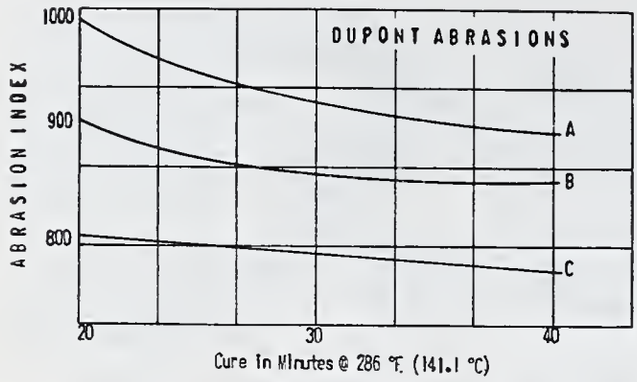

FIGURE 9. PHYSICAL TEST DATA FOR ZINC OXIDES A, B, AND C

$$\text{Abrasion index} = \left(\frac{\text{cc. loss per hp.-hr. for ZnO A}}{\text{cc. loss per hp.-hr. for comparative ZnO}}\right) \times 1000$$

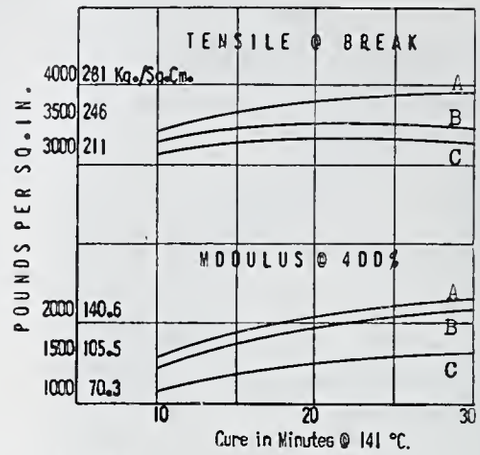

FIGURE 10. PHYSICAL TEST DATA

Zinc oxides A, B, and C

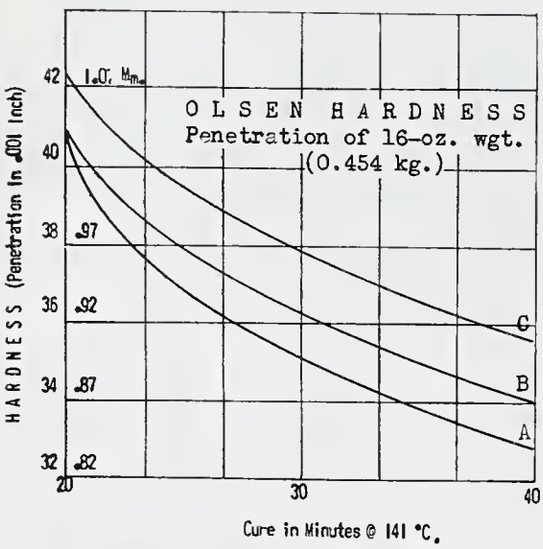

FIGURE 11. PHYSICAL TEST DATA

Zinc oxides A, B, and C

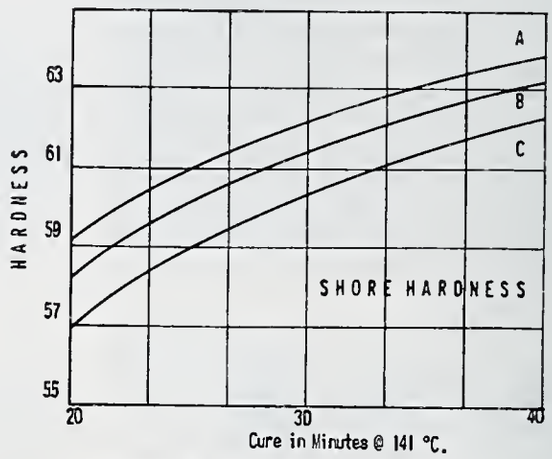

FIGURE 12. PHYSICAL TEST DATA

Zinc oxides A, B, and C

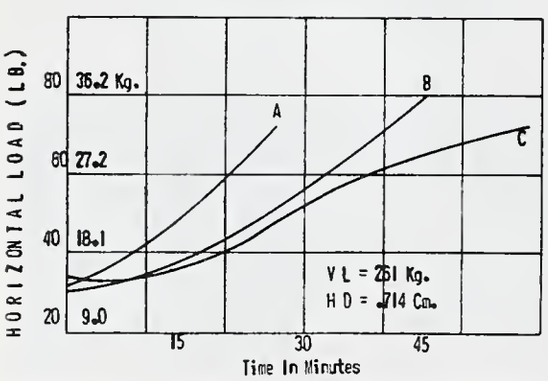

FIGURE 13. CONSTANT HORIZONTAL DEFLECTION TEST

Zinc oxides A, B, and C

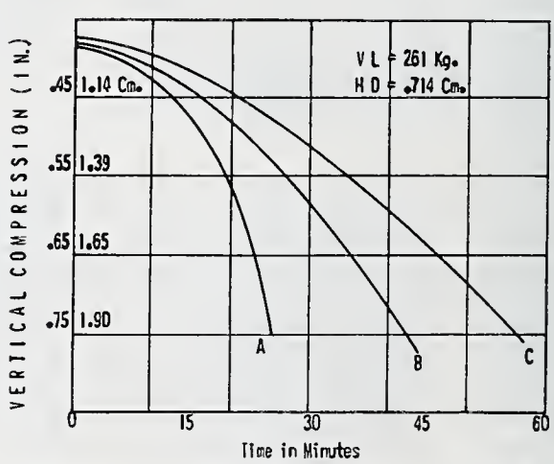

FIGURE 14. CONSTANT HORIZONTAL DEFLECTION TEST

Zinc oxides A, B, and C

pression (decrease in height of test specimen) which would normally indicate a softening of the stock. Figure 13, however, shows that the compound actually stiffens during test, which indicates that the flattening is due not to a softening of the stock, but probably to a continuous change in the permanent set of the stock as the test progresses.

CONSTANT VERTICAL COMPRESSION TEST. Figure 16 shows a modification of the constant horizontal deflection test. In this case the vertical compression was maintained constant and the vertical load was measured on a platform scale similar to the horizontal load scale. It is interesting to note that although the vertical compression and horizontal deflection were held constant, the horizontal load increased during the test. These data indicate that the increase in horizontal load is not due to any change in shape of the specimen during the test, but to a structural change which takes place in the rubber.

STEPPED INCREASE HORIZONTAL LOAD TEST. Figure 17 and Table III show data on the various zinc oxides when compared by the stepped increase horizontal load test. The conditions of horizontal loading are exactly the same for the three stocks, and deflections are dependent on modulus and stiffness of the compounds. The temperature at the center of the test specimen has been plotted against time. Zinc stocks B and C show a rapid increase in temperature at the start of the test due to greater deflection produced by the horizontal load on these softer stocks. (Figures 11 and 12).

In this method of testing the stock containing coarse particle size zinc oxide C does not resist breakdown as well as stocks containing zinc oxides A and B.

EFFECT OF CURE. The effect of cure on breakdown, when specimens are tested by the constant horizontal deflection test method, is shown on Figures 18 and 19. The optimum cure as regards time required to break down a specimen is 85 minutes, while the optimum cure, as regards maximum tensile strength, is only 15 minutes. In general, the undercures suffer greater initial vertical compression and require more horizontal load at the finish of the test than either the optimum or overcures.

EFFECT OF CHANGES IN VOLUME LOADING. Results of tests on rubber compounds with a variation in the zinc oxide content, when tested under constant horizontal deflection

test conditions, are shown in Figures 20, 21, and 22. The zinc oxide in the formula, Table II, was varied by 5 volumes either side of the standard, which is 26.7 volumes on 100 parts (by weight) of rubber. To maintain the same horizontal deflection, the higher loaded stocks require greater horizontal load or deflecting force than the lower loaded stocks.

In Figure 22 the horizontal load is plotted against the increase in vertical compression with the time intervals noted on the curves. If the area under the curve be considered as a measure of energy expended, the higher volume loadings require more work to cause failure.

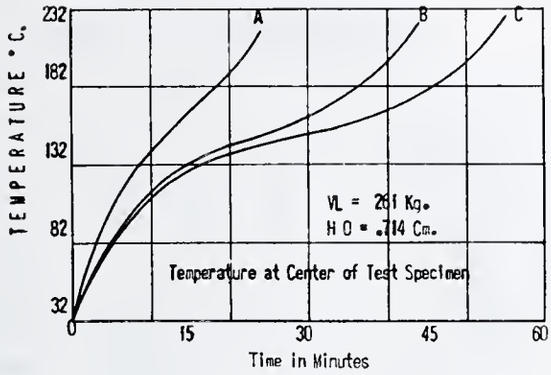

FIGURE 15. CONSTANT HORIZONTAL DEFLECTION TEST

Zinc oxides A, B, and C

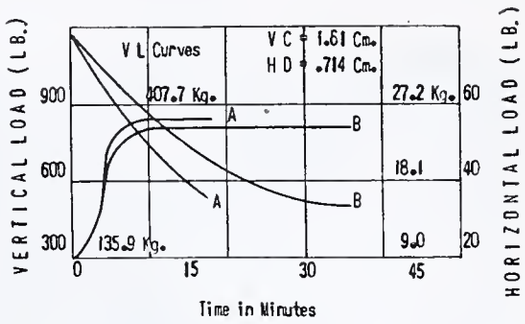

FIGURE 16. CONSTANT VERTICAL COMPRESSION TEST

Zinc oxides A and B

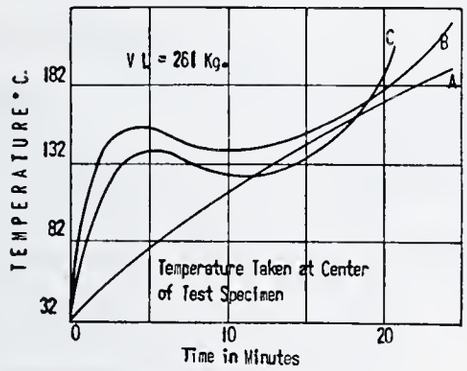

FIGURE 17. STEPPED INCREASE HORIZONTAL LOAD TEST

Zinc oxides A, B, and C

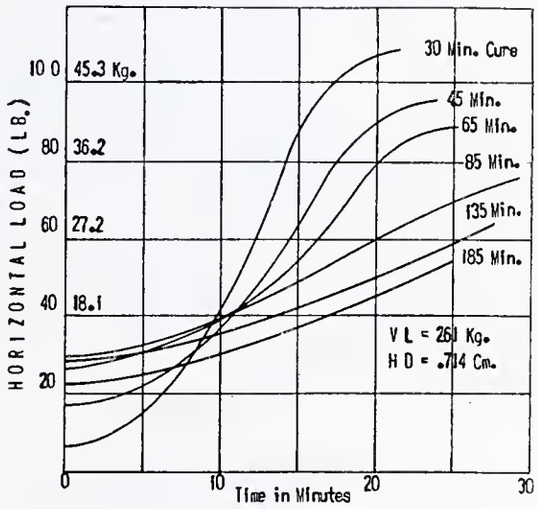

FIGURE 18. EFFECT OF CURE

Zinc oxide A

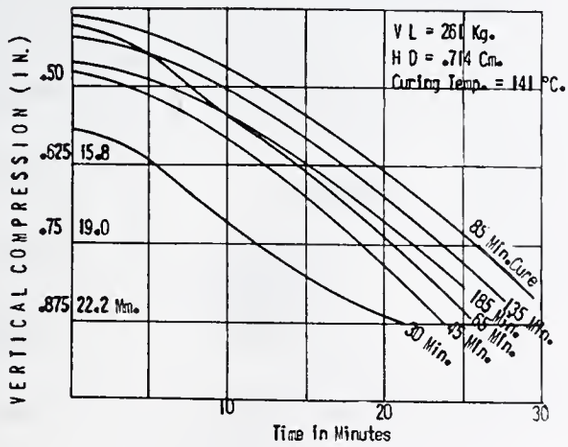

FIGURE 19. EFFECT OF CURE

Zinc oxide A

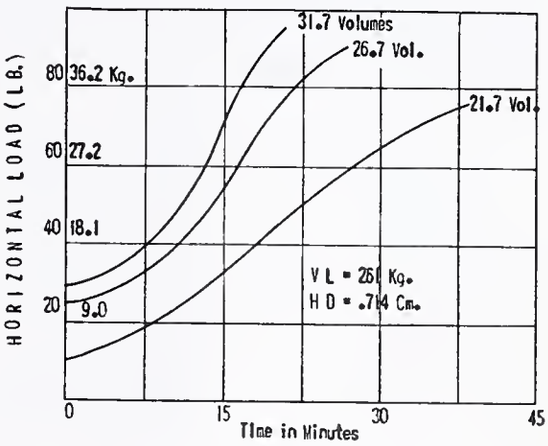

FIGURE 20. CHANGES IN VOLUME LOADING

Zinc oxide A

EFFECT OF CHANGES IN VERTICAL LOAD. Figure 23 shows that an increase in vertical load on a specimen results in a shortening of the time required to produce failure. With an increase in vertical load on the specimen, less horizontal load is required at the start of a test. At the finish, however, a greater horizontal load is required for the same horizontal deflection.

EFFECT OF CHANGES IN HORIZONTAL DEFLECTION. Breakdown is produced in a rubber specimen by running under vertical load and horizontal deflection. An increase in horizontal deflection subjects the specimen to greater stresses and shortens the time required for a test. Conversely, a decrease in the deflection is reflected by a decrease in flexing force and increase in running time. Results of tests using different horizontal deflections are shown on Figure 24. Although the difference between the low and medium deflections is the same as that between the high and medium deflections, the variation in the flexing load–time rate is approximately 4 to 1.

COMMERCIAL STOCKS

The machine, to be of commercial value, must show good correlation between laboratory and service tests. To study this correlation the authors obtained from several rubber companies carcass and solid tire stocks with ratings of good and poor as regards resistance to blowout in service. The laboratory tests show that excellent correlation is obtained. Results obtained on some representative commercial stocks are shown in Figures 25 to 30.

CARCASS STOCKS. Two carcass stocks were compared by the constant horizontal deflection test method, as it was felt that this method of testing would most nearly approach

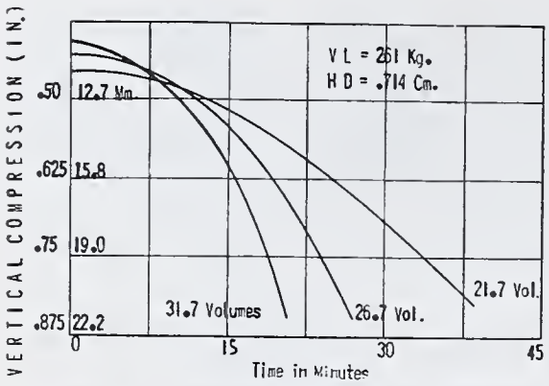

FIGURE 21. CHANGES IN VOLUME LOADING

Zinc oxide A

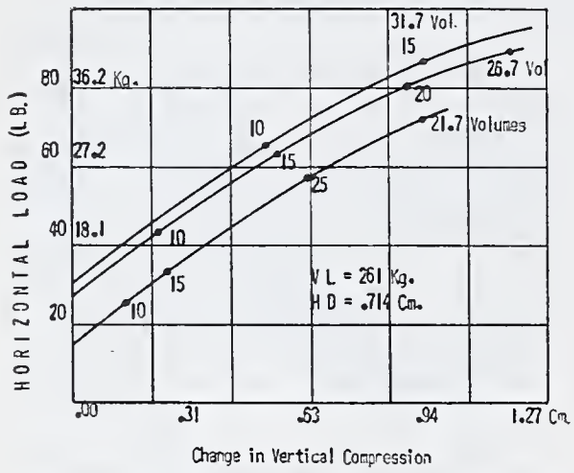

FIGURE 22. CHANGES IN VOLUME LOADING

Zinc oxide A

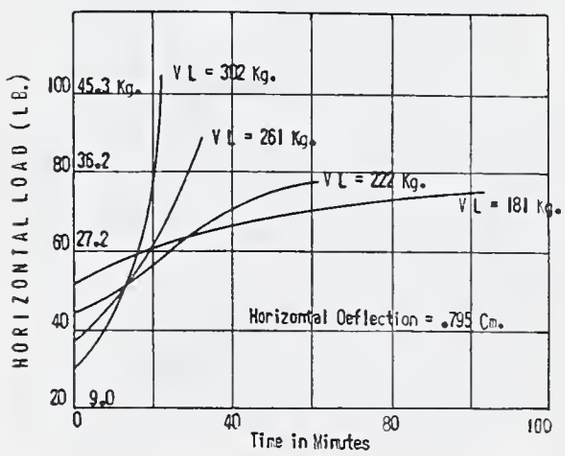

FIGURE 23. EFFECT OF CHANGES IN VERTICAL LOAD

Zinc oxide B

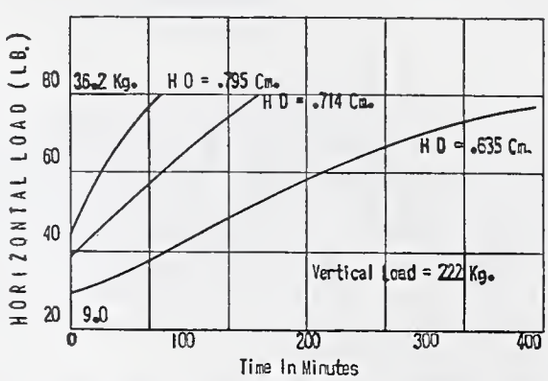

FIGURE 24. VARIATION IN HORIZONTAL DEFLECTION

Zinc oxide B

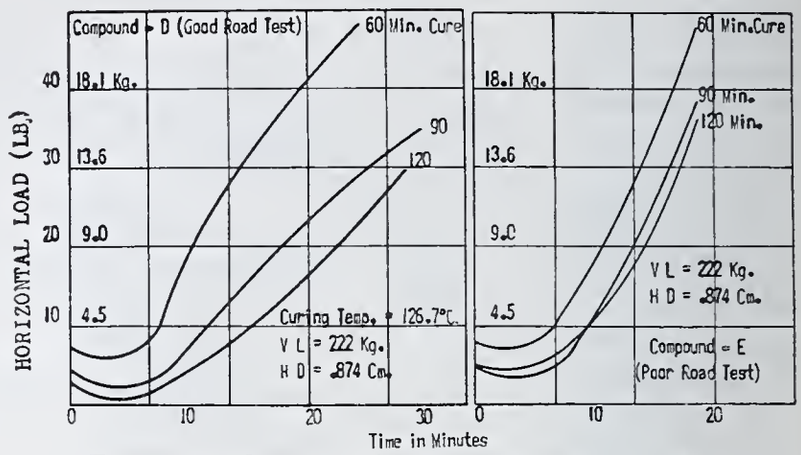

FIGURE 25. CONSTANT HORIZONTAL DEFLECTION TEST

Commercial carcass compound

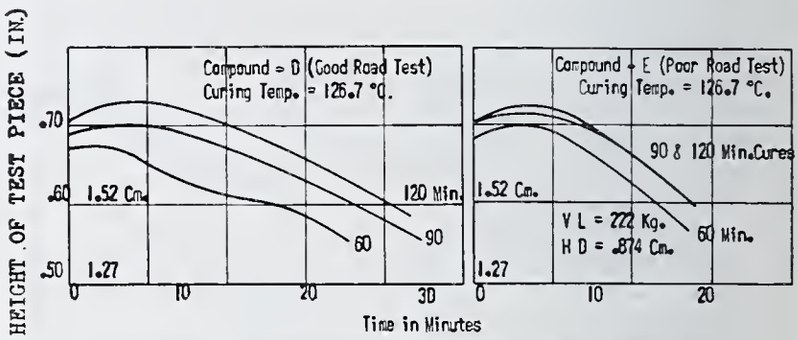

FIGURE 26. CHANGE IN HEIGHT OF TEST SPECIMEN

Commercial carcass compound

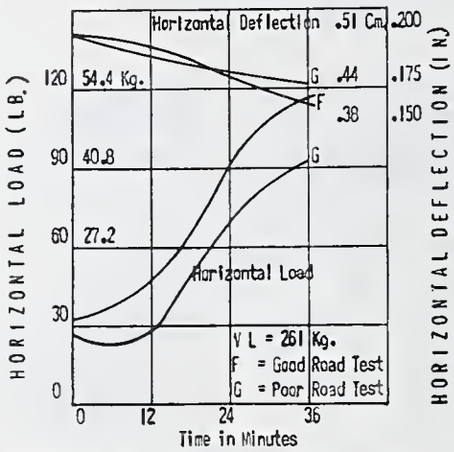

FIGURE 27. CONSTANT HORIZONTAL DEFLECTION TEST

Commercial solid tire stocks

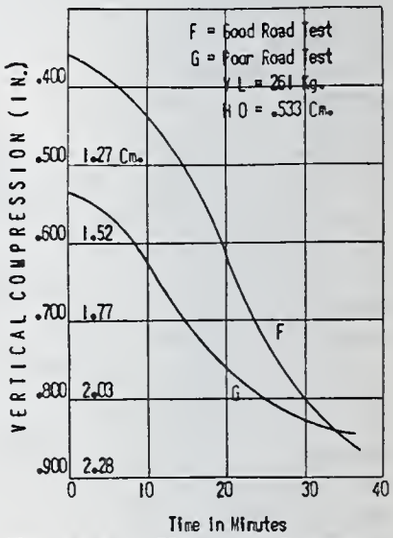

FIGURE 28. VERTICAL COMPRESSION TEST

Commercial solid tire stocks

actual service conditions. Under, optimum, and overcures were made on each stock. With essentially the same applied flexing force, compound D (good road test) resists failure for a longer time than compound E (poor road test), which checks the manufacturers' road tests.

SOLID TIRE STOCKS. The results of tests on two solid tire stocks, F (good) and G (poor), when run by the constant horizontal deflection test method are shown on Figures 27 and 28. These two stocks would be rated equal if considered on a time basis alone, but when the horizontal load or deflecting force is a consideration, stock F is decidedly superior, since it runs for the same length of time under a much greater load. On Figure 28 the vertical compression is plotted against time. If the time for a 0.762-cm. (0.30-inch) drop in vertical compression is used as the end point, stock G

reaches this in 35 minutes, and stock F in 23 minutes. It is evident that machines which evaluate on vertical compression and time only give results which may be greatly in error.

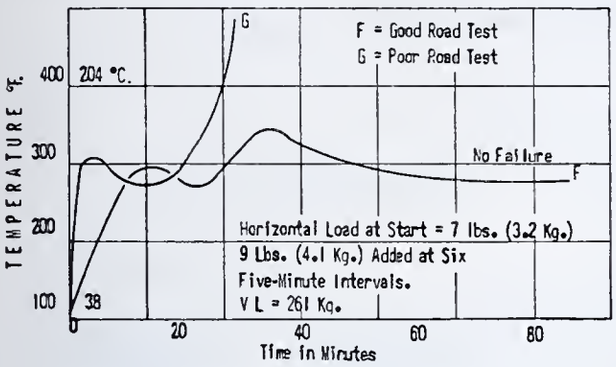

FIGURE 29. STEPPED INCREASE HORIZONTAL LOAD TEST

Commercial solid tire stocks

To duplicate service conditions as nearly as possible, it was felt that the stocks should be tested under the same loading conditions. The deflections would then be dependent on the modulus and stiffness of the compounds. The stepped increase horizontal load test was used and temperatures were taken at the center of the specimen and plotted against time (Figure 29). Both specimens were subjected to the same system of loading, which was 3.2 kg. (7 lb.) at the start increased by 4.1 kg. (9 lb.) at six 5-minute intervals. Stock G failed in 30 minutes, while stock F did not fail even after 90 minutes of testing. At the end of 90 minutes the temperature was dropping, indicating that failure due to heat was impossible.

The stocks were then compared under the matched horizontal load conditions of testing. Both stocks were first run in the regular way, as shown on Figure 27, with a vertical load of 261 kg. (575 lb.) and a horizontal deflection of 0.533 cm. (0.210 inch). Stock G was again tested and the horizontal load adjusted by means of the handwheel to match the greater load of stock F. Stock G failed in considerably less

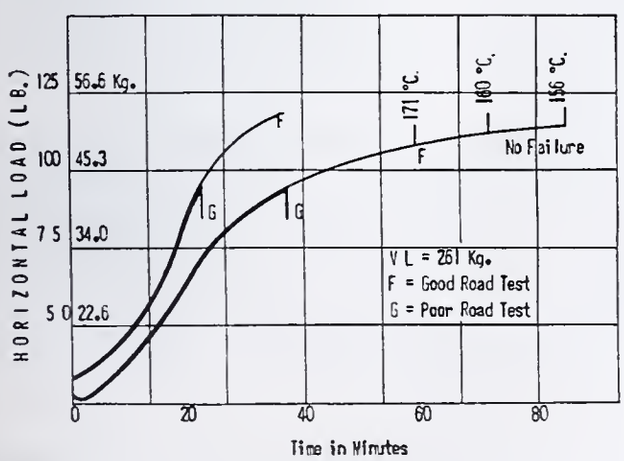

FIGURE 30. MATCHED HORIZONTAL LOAD TEST

Commercial solid tire stocks

time than stock F, which again checks the manufacturers' road tests. Stock F was again tested and the horizontal load adjusted to match the lesser load required by stock G. Stock F withstood the less severe conditions and the specimen started to decrease in temperature after 60 minutes, indicating that no failure due to heat would occur. This test is recorded on Figure 30.

SUMMARY

A new machine for evaluating breakdown characteristics of rubber compounds, described above, not only measures the flexing forces at all times, but also indicates the point of initial failure, accurately, before complete destruction of the test specimen takes place. The theoretical value of the machine has been revealed by the indication of an unexpected structural change which takes place in the rubber during flexing. This change manifests itself in a marked stiffening of the stock which increases until initial failure occurs. The practical value of the machine has been demonstrated by its ability to simulate different types of service conditions, as shown by the excellent correlation of the authors' tests with the manufacturers' road tests on commercial compounds.

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(2) Cooper, *Ibid.*, Anal. Ed., 5, 350–1 (1933).
(3) Perrott, G. St. J., and Kinney, S. P., *J. Am. Ceramic Soc.*, 6, 417–25 (1923).
(4) Schopper, Louis, *Catalog* 415, p. 25, Leipzig, Germany; American agent, Testing Machines, Inc., New York, N. Y.

RECEIVED September 15, 1934. Presented before the Division of Rubber Chemistry at the 88th Meeting of the American Chemical Society, Cleveland, Ohio, September 10 to 14, 1934.

Wash Bottle for Quantitative Work

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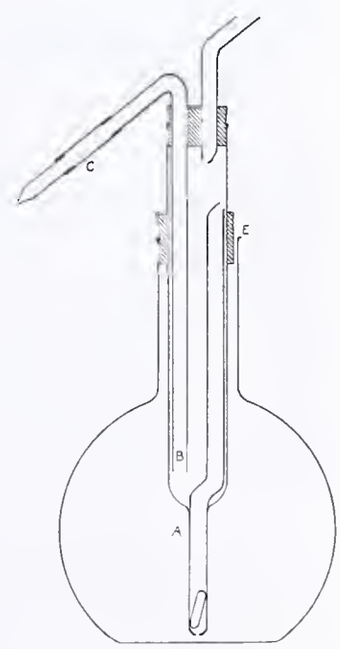
IT FREQUENTLY happens in analytical work that a precipitate must be washed or transferred from one container to another with a limited quantity of reagent. By means of the device illustrated, a measured amount of liquid may be directed in such a way as to aid in stirring up and dislodging the precipitate.



The tube *A* is sealed into the bottom of the inner reservoir and the end cut off at right angles. A small rounded section of glass rod is dropped into the inverted tube and the end carefully and evenly heated with a small hot flame until the contracting glass has almost sealed the opening. This simple valve will permit pressure to be built up within the inner reservoir, so that its contents may be blown out. It will also prevent the flow of liquid from the outer to the inner reservoir following sudden changes in pressure. A small vent, indicated at *E*, may be cut into the stopper in case too much air escapes through the valve.

The diameter of the inner reservoir and the depth to which the delivery tube, *B*, extends, govern the volume of liquid expelled at any one time. The inner reservoir is filled by pinching the rubber connection, *C*, thus shutting off the delivery tube, and applying suction at the mouthpiece. Excess liquid will drain back into the inner reservoir. It is emptied in the usual manner, care being taken not to incline the wash bottle too much.

RECEIVED October 31, 1934.

Photronic Photoelectric Turbidimeter for Determining Hydrocyanic Acid in Solutions

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HYDROCYANIC acid is used extensively in certain localities as a plant fumigant. Because of differences obtained when fumigating citrus trees, experiments were conducted to determine the amounts of hydrocyanic acid that were absorbed by citrus foliage under varying environmental conditions. The Liebig silver nitrate method was used for determining the amounts of hydrocyanic acid that were recovered, but this method, which calls for the titration of the hydrocyanic acid in alkaline solution in a flask or beaker, was not sufficiently accurate when dealing with such small amounts of hydrocyanic acid.

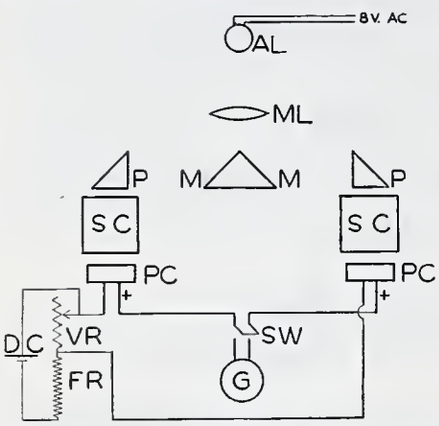

Figure 1. Diagram of Photronic Photoelectric Turbidimeter

8V.AC. 8-Volt alternating current
AL. Auto lamp, 32 candlepower
ML. Movable lens
M, M. Mirrors
P, P. Prisms
SC, SC. Solution cells
PC, PC. Weston photronic cells
VR. Decade resistance box, 0.1 ohm steps
FR. Fixed resistance, 250,000 ohms
DC. 1.5-Volt dry cell
SW. Switch, double-pole single-throw
G. Galvanometer

Taking a suggestion from Cupples (*1*), a specially devised visual nephelometric apparatus was then constructed and used in a dark room. This method gave decidedly better results but was far from satisfactory. In order to obviate these troubles, after a few tests had been made with the photronic colorimeter described by Wilcox (*2*), it was decided to devise and construct a photronic photoelectric turbidimeter.

The authors' turbidimeter, which serves equally well as a colorimeter, has been found very satisfactory. However, if the apparatus were to be used as a colorimeter it would be well to use a storage battery in place of the dry cell to insure a constant e. m. f. across the potentiometer. It is the purpose of this paper to give a description of the turbidimeter and also enough data to prove its efficiency. Since in these tests the apparatus has been used as a turbidimeter only, it will be referred to as such in this paper.

Photronic Turbidimeter

The construction of the photronic turbidimeter is diagrammatically represented in Figure 1.

A transformer is inserted between the regular laboratory convenience outlet and the 32-candlepower auto lamp, *AL*, which reduces the voltage to 8 volts. The lamp is attached to a heavy metal base (duralumin) to prevent any possible warping effects due to changes in temperature. The metal base is movable to permit focusing.

The lens, *ML*, which throws parallel rays of light on the mirrors, *M, M*, is mounted in a rectangle of brass 1.1 cm. thick. By means of a threaded micrometer attachment the lens may be moved to the right or left, in order to throw the desired amount of light on each of the mirrors. These mirrors were made by a new process which calls for the evaporation of an alloy in vacuum, and are called "panchro" mirrors. They are excellent for this purpose because their nontarnishing front surface has a fairly high coefficient of reflection, which is uniform for all colors of the visible spectrum. The mirrors, which are on very thin glass, are cemented to a right-angle prism. This prism and the two right-angle prisms, *P, P*, are attached to a rectangle of brass 1.1 cm. thick, which is firmly attached to the baseboard of the apparatus.

SC, SC are solution cells, preferably having two opposite, flat, polished walls parallel to each other. *PC, PC* are two paired, Model 594 Weston photronic photoelectric cells. (The energy output of this type of photoelectric cell is a function of the intensity and frequency of the light which falls upon its sensitive surface.) *G* is a box-type lamp and scale galvanometer, sensitive to 0.63 megohm. The positive terminals of the photronic cells are connected directly to the galvanometer leads. *SW* is a switch with which to operate the galvanometer circuit. The negative terminals of the photronic cells are connected to the potentiometric arrangement *VR* + *FR*. *VR* is a decade resistance box with a maximum resistance of 9999.9 ohms, in 0.1-ohm steps. *FR* is a 1-watt 250,000-ohm fixed resistance. *DC* is a 1.5-volt dry cell. When *VR* is set at zero, *DC* is shunted by *FR*. With *VR* at zero and *SW* closed, the illumination may be so adjusted by the movable lens, *ML*, that there will be no current flowing through the galvanometer.

The wiring of the apparatus described has proved to be very satisfactory. It is known that there is some polarizing effect on the photronic cells when current is allowed to flow through them. In this system the cells are not shunted, but are directly opposed to each other. The system is potentiometrically balanced and calibrated so that there is no flow of current through the cells and therefore no polarization. The conditions described permit the cells to act at maximum sensitivity.

In most of the photoelectric turbidimeters and colorimeters which have been described, only one photoelectric cell has been used. The authors have used two in order to exclude or reduce to a minimum the effects of possible fluctuations in line or battery voltage, possible errors due to light-effect changes in colored solutions or fatigue of the photronic cells, possible error in determining the end point in the presence of both color and turbidity in the solutions (*3*), and to eliminate the need for constructing a reference standard.

Figure 2 is a photograph of the photronic turbidimeter.

The galvanometer, resistance box, dry cell, variable resistance, and transformer are accessory and are not shown. The wiring indicated in Figure 1 is all on the under side of the base. The elevation to the right is the lamp housing which has a louvered top and base to permit ventilation. The two low elevations are the light tunnel (right) and the housing for the mirrors and prisms (left), with the movable lens and its micrometric adjuster between. The high elevation to the left contains two compartments, each 7.5 × 10.2 × 13.3 cm. high, in which the solution cells are placed. The single cover for these two compartments is hinged at the back and in order to exclude external light is always kept closed while readings are being made. The two photronic cells are shown at the extreme left, mounted in brass cylinders 4.5 cm. long. All interior surfaces are flat black.

Operation of Photronic Turbidimeter

The first step in the operation of the photronic turbidimeter is to insert the solution cells, each containing a duplicate aliquot of the solution to be tested. These cells should be of such a height that they will take an aliquot which is large enough to bring the surface of the solution well above the upper edges of the photronic cells. This is important. If the surface of the solution is too low, light passing upward will be reflected onto the sensitive surface of the photronic cells and thus give an erroneous reading, especially at the end of titration when the surfaces of the liquids in the two solution cells would be of unequal heights.

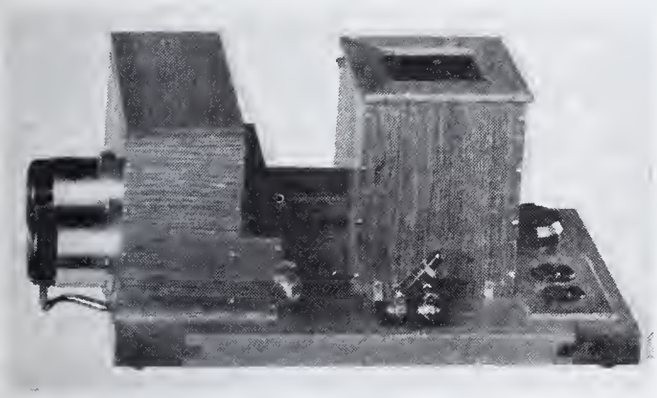

Figure 2. Photograph of Turbidimeter, without Accessories

When the solution cells have been inserted, the lid has been closed, and *VR* set at zero, the switch which operates both turbidimeter and galvanometer lamps is turned on. After the photronic cells and the galvanometer have become approximately adjusted (perhaps 10 to 15 minutes) the switch, *SW*, is closed and the light beam on the galvanometer scale is brought to the null point, by shifting the movable lens so that the light falling on the photronic cells is properly divided. As soon as the photronic cells have become completely adjusted and the galvanometer beam remains permanently at the null point, titration is begun.

A quantity of silver nitrate is added to one of the solution aliquots, thoroughly stirred, the lid closed, and the switch thrown in. If there is no deflection from the null point, the process is repeated until a deflection is obtained. The deflection signifies that the end point has been reached—that is, that silver cyanide has been precipitated, that the solution has become turbid, and that, as a result, the energy output of the corresponding photronic cell has been decreased. The nature of the precipitate particle is not a factor in these measurements, because it is the beginning and not the degree of turbidity which is being determined. The size of the particles causing the slight turbidity in the solution before titration was begun was such that there was no appreciable settling between the time of stirring and the taking of the reading. The amount of hydrocyanic acid in the aliquot is computed from the amount of silver nitrate necessary to produce initial turbidity. This completes the operation, unless one wishes in a general way to determine the increase in turbidity as additional amounts of silver nitrate are added. In this case sufficient resistance from *VR* is added each time to bring the galvanometer beam back to the null point. The variable resistance would be used also when the instrument was being employed as a colorimeter.

The usual rules of titration, such as those relating to stirring and the time element, not only apply here but their effect can be more easily detected with this instrument than by the usual methods.

Results

Accurate determinations of small amounts of hydrocyanic acid could be made with the photronic turbidimeter even though the solutions were not clear before titration began. For example, on adding like amounts of liquid hydrocyanic acid to clear alkaline solutions and to alkaline solutions that had been made light yellow and slightly turbid by immersing and shaking the leaves in them, practically the same titration end-point readings were obtained.

With the photronic turbidimeter determinations could be made which were accurate to within 0.00054 mg. of hydrocyanic acid, but for the authors' purpose, determinations to within 0.027 mg. were considered sufficiently accurate.

Table I shows the accuracy with which given amounts of hydrocyanic acid could be recovered from the solutions. The presence of color and slight turbidity in the solutions before titration was begun did not materially affect the accuracy of the end-point reading.

Table I. Recovery of Hydrocyanic Acid from Clear and Non-clear Solutions

HCN Used	HCN Recovered: Clear solution	HCN Recovered: Non-clear solution[a]
Gram	*Gram*	*Gram*
0.001456	0.001458	0.001458
0.01550	0.015490	0.015486
0.03120	0.031185	0.031185
0.03070	0.030691	0.030688
0.03140	0.031382	0.031377

[a] Solution which had been filtered after immersing and shaking the leaves in it.

Table II further indicates what small amounts of hydrocyanic acid may be detected and measured with the photoelectric turbidimeter. The figures in columns 2 and 3 represent the amounts of hydrocyanic acid in samples of air aspirated from the fumatorium 2 minutes after the beginning and 2 minutes before the close of the fumigation period. The air and leaf samples represent equivalent volumes. The actual amount of hydrocyanic acid to which the leaves had access in the fumatorium was 3528 times as much as is indicated in the figures in column 2. The variations in the amounts of hydrocyanic acid in the fumatorium and in the amounts absorbed by the different lots of leaves will be explained when a more detailed report is published.

Table II. Accumulation of Hydrocyanic Acid in Fresh, Mature Valencia Orange Leaves during 45-Minute Fumigation Period

Test	Hydrocyanic Acid Recovered: Fumatorium air, sample 1	Hydrocyanic Acid Recovered: Fumatorium air, sample 2	Hydrocyanic Acid Recovered: 200-gram lots of leaves	Ratio: Column 4: column 2	Ratio: Column 4: column 3
	Gram	*Gram*	*Gram*		
1	0.0004176	0.0002376	0.01728	41.4	72.7
2	0.0002742	0.0002020	0.01584	57.8	78.4
3	0.0002953	0.0002304	0.01368	46.3	59.4
4	0.0002590	0.0001940	0.01656	63.9	85.4

Acknowledgment

The authors with to express their appreciation to H. W. Edwards, of the University of California at Los Angeles, for making the "panchro" mirrors, and to H. H. Bliss, of the Riverside, Calif., Junior College, for assistance in working out a satisfactory electrical circuit for the turbidimeter.

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Apparatus for Control of Pressure in Distillation

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THE desire of chemists for better methods of controlling pressure has led to many improvements in this type of apparatus. Huntress and Hershberg (*2*) give a very comprehensive bibliography on controlling low pressure during distillation. None of the commonly used devices are without certain faults. The widely used method of using an electromagnetically operated flutter valve (*1*, *4*) against a capillary leak, being independent of any specific mode of maintaining vacuum, seemed a logical starting point for this work. The recent paper by Palkin and Nelson (*5*) describes what appears to be an extremely fine control mechanism for this purpose.

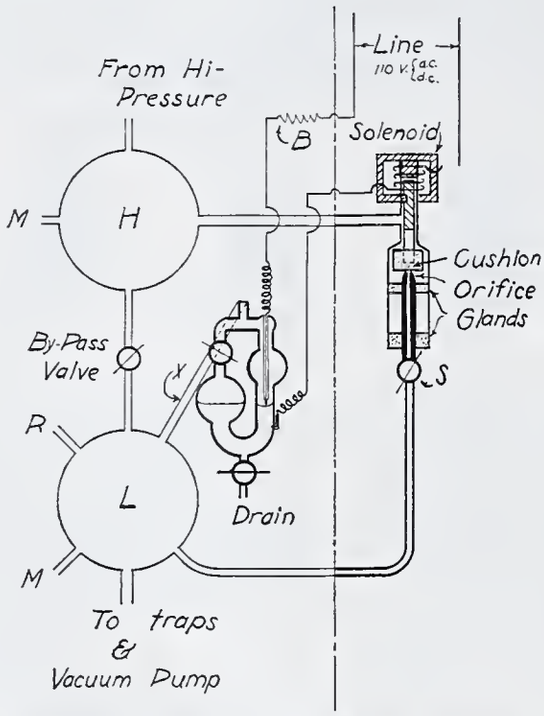

Figure 1. Schematic Drawing Showing Valve in Conjunction with Appurtenances

A previous paper by the author (*3*) describes the use of an inexpensive valve. The purpose of the present paper is to describe a highly simplified and improved form of valve, whose parts may be easily duplicated. The solenoid valve has certain advantages: It is positive in action, permits smooth regulation of pressure (±0.015 mm.), is universally adaptable to vacuum and pressure, is available for closed systems of inert gases, and works on lighting socket power without relay. This particular valve, moreover, experiences very little wear and is practically free from corrosion, a factor of no little importance in the chemical laboratory.

Figure 1 illustrates the principle upon which this valve operates. Control of the capillary leak from a higher to a lower pressure system is managed by automatic activation of the solenoid by means of the Hershberg and Huntress sulfuric acid manostat (*1*).

The activated solenoid lifts an encapsulated iron core with rubber pad and permits a flow of gas. Interruption of the coil current permits a gravitational closing of the capillary. A stopcock, *S*, or needle valve below the capillary leak permits the rate of leak to be adjusted up to the limit of flow through the particular capillary used. Additional flow is accomplished by the bypassing of the gas through suitable control either by stopcock or needle valve.

The solenoid proper was made to specifications for the author by the Struthers Dunn Company of Philadelphia, and given a serial number of CX1388. This solenoid is properly sized to fit down over a 12-mm. outside diameter Pyrex glass tube. The armature was conveniently made by slotting longitudinally and circumferentially a 4- to 5-mm. iron rod 3 cm. in length to reduce eddy currents. This armature is enclosed in a thin-walled glass capsule whose outside diameter clears readily the inside diameter of the 12-mm. outside diameter glass tube previously mentioned. A No. 0 rubber stopper, half bored, which is continually raised and lowered as the pad sealing the capsule must be boiled in alkali (*4*). This pad seats itself by gravity upon a capillary orifice drawn out and ground plane. The capillary is retained by two rubber glands (simply slices of one-hole rubber stoppers correctly dimensioned).

Other valves and seats that were tried were: ground glass to ground glass, and rubber plugs more nearly the size of the capillary leak. The former, although reasonably tight, required too much lifting force, while the latter, having a high center of gravity, failed to give reliable seating.

H and *L* are Pyrex flasks serving respectively as high- and low-pressure buffer chambers, with outlets *M* to suitable manometers; *B* is a 25-watt lamp acting as a ballasting resistor; *R* is from the receiver of the still or other apparatus whose pressure is to be regulated. The valve proper is thus shown in its relation to its appurtenances, which may be existing equipment.

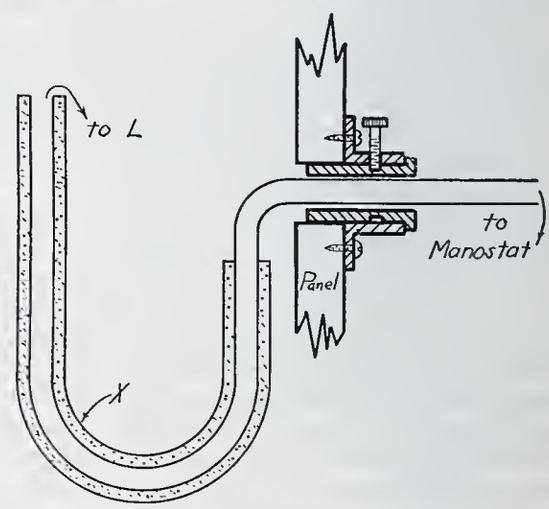

Figure 2. Detail of Improved Swivel

The writer considers the Hershberg-Huntress sulfuric acid manostat a great improvement over the ordinary differential manometer employing mercury. In the set-up now in use in this laboratory a simplified swivel for the manostat was installed, replacing their ground-steel joint (*1*, Figure 4, *K*).

This new brass swivel (Figure 2) is simply two concentric tubes, the mutual rotation of which may be arrested by a set-screw through the outer tube bearing into a groove cut encircling the inner tube. The outer brass tube is mounted to a vertical panel by means of the flange, while the Pyrex tube of the manostat, passing through the inner brass tube, is cemented thereto with sealing wax. Connection is then afforded by a short length of pressure tubing, *X;* furthermore tube *H* (*1*, Figure 4) may be sealed in, necessitating the addition of a stopcock (Figure 1) for draining and refilling, which if always covered with liquid helps

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seal and render leaks the more easily detected. This swivel seems to be simpler and more positive than the one described by Palkin and Nelson (*5*). Control of regulation by this valve was so good as to cause but a slight ripple on the surface of the sulfuric acid in the manostat. The effect upon the mercury level would certainly not be greater than ±0.015 mm.

When dispensing with relays, no difficulty due to the increased current flowing through the manostat was experienced in many hours of operation. All work was done with alternating current, but with direct current, inasmuch as both electrodes are in the same arm, all electrolytic gases will doubtless be reunited at the interrupting electrode as they seem to be by the alternating current. (Even if all electrolytic gases were to enter the system at *L*, Figure 1, the quantity formed as calculated for 1 mm. pressure by Faraday's law and Boyle's law would be less than 1 cc. per minute, a value negligible compared to the capacity of the pump.)

An apparatus of this type has been in use at the laboratory at Rutgers University since July, 1933. It has proved capable of performing complete distillations at predetermined pressures. It is quiet in operation and exceedingly simple.

Acknowledgment

Many thanks are due to the following for technical suggestions: P. A. Hoover, D. L. Cottle, P. V. McKinney, all of Rutgers University; E. H. Huntress of the Massachusetts Institute of Technology; and J. A. Doremus of Lafayette College.

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Application of the Glass Electrode to Dairy Products

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THE common methods of measuring the pH of milk and its products are the hydrogen electrode, the quinhydrone electrode, and the colorimetric. The glass electrode and the stick antimony electrode have not been accepted as standard methods for dairy products.

The purpose of this investigation was to determine the pH of whole milk, buttermilk, cream, commercial ice cream mix, and butter; by glass, quinhydrone, hydrogen, and stick antimony electrodes.

Procedure

The electrical potentials were measured by a vacuum-tube potentiometer of design similar to that of Rosebury (*8*), who used a General Electric FP. 54 vacuum tube and a Leeds & Northrup type 7651 potentiometer. The circuit used for this investigation was modified somewhat to permit the use of a type K Leeds & Northrup potentiometer. A four-pole double-throw switch was used for S_2, connected so as to short-circuit the galvanometer terminals of the type K when the potential readings were being made.

The glass electrode was of the bulb type, made of 015 Corning glass according to the method of Robertson (*7*). The bulb, after being blown, was filled with 0.1 *N* hydrochloric acid and was aged in distilled water for about a month. The cell used was

$$\text{Hg} \;|\; \begin{matrix}\text{HgCl}\\ \text{KCl (sat.)}\end{matrix} \;|\; \begin{matrix}\text{Unknown}\\ \text{solution}\end{matrix} \;\underset{\text{Glass membrane}}{|||}\; 0.1\,N\,\text{HCl} \;|\; \begin{matrix}\text{HgCl}\\ \text{KCl (sat.)}\end{matrix} \;|\; \text{Hg}$$

The bulb was washed thoroughly with distilled water before each determination. The e. m. f. usually increased during the first two or three readings, after which constant values were obtained. The electrode was then checked with a phthalate buffer of pH 5.697 as determined by hydrogen and quinhydrone electrodes. After checking the calibration of the glass electrode with the buffer, another determination was made to make sure that the asymmetry potential of the glass membrane was still constant. The change of asymmetry potential which sometimes occurred during the first two or three readings was probably due to the formation of a thin fatty film over the glass membrane.

Quinhydrone electrodes were prepared from platinum foil and plated with gold as recommended by Popoff, Kunz, and Snow (*6*). To each 50-ml. sample of dairy product 0.2 gram of Eastman's quinhydrone was added and the mixture was stirred thoroughly before readings were taken.

The Hildebrand electrodes consisted of platinum foil 1 cm. square, coated with platinum black as recommended by the Leeds & Northrup Company (*3*). These electrodes were used with electrolytic hydrogen purified by passing through solutions of mercuric chloride, alkaline permanganate, alkaline pyrogallol, dilute sulfuric acid, and water. The rate of flow was controlled as suggested by Duncombe (*2*).

The Bailey electrode was used as directed by Bailey (*1*). Antimony electrodes were cast from Mallinckrodt's c. p. anti-

Table I. pH Determinations

(At 25° C.)

	Glass	Quinhydrone (Gold)	Hildebrand	Antimony
		Pasteurized whole milk		
	6.585	6.589	6.585	6.94
	6.587	6.586	6.583	6.95
	6.587	6.588	6.583	6.96
	6.585	6.586	...	6.95
Av.	6.586	6.587	6.584	6.95
		Pasteurized buttermilk		
	4.305	4.302	4.304	4.84
	4.305	4.304	4.301	4.84
	4.307	4.305	4.304	4.87
	4.307	4.304	...	..
Av.	4.306	4.304	4.303	4.85
		Pasteurized single cream		
	6.603	6.600	6.605	6.90
	6.601	6.598	6.605	6.88
	6.603	6.600	6.603	6.98
	6.603	6.600	6.605	6.88
Av.	6.603	6.600	6.605	6.91

Table II. pH Determinations

(At 25° C.)

	Glass	Quinhydrone (Gold)	Hildebrand	Bailey	Antimony
		Commercial ice cream mix			
	6.614	6.617	6.615	6.598	7.09
	6.614	6.617	6.615	6.609	7.05
	6.615	6.615	6.615	6.613	7.08
	...	6.617	6.617	...	7.07
Av.	6.614	6.616	6.615	6.607	7.07
		Butter serum			
	5.995	6.003	6.001	5.994	6.64
	5.993	6.003	5.990	5.993	6.64
	5.993	6.005	5.994	5.994	6.64
Av.	5.994	6.004	5.995	5.994	6.64

mony. The potential readings were taken at the end of five minutes as specified by Parks and Beard (*5*). The butter serum was prepared according to the method of Nissen (*4*).

The results for the different electrometric methods are given in Tables I and II.

Discussion

The hydrogen-ion concentration of dairy products may be determined by the glass electrode, the quinhydrone electrode, or the hydrogen electrode with an accuracy which is within experimental error.

A decided drift occurs when platinum electrodes are used with quinhydrone, and is especially noticeable with ice cream mix and butter serum. This drift, however, may be eliminated by the use of gold electrodes.

The stick antimony electrode determinations were from 0.307 to 0.646 pH units higher than those of the glass electrode. The errors appear to increase with high concentration of serum solids and with the lactic acid content. The effects upon the stick antimony electrode of solutions containing citric acid, lactic acid, and lactose are emphasized in the following experiments.

A solution containing 0.235 gram of citric acid per 150 ml. was neutralized with sodium hydroxide to a pH of 3.72 as measured by the glass electrode. This solution showed a pH of 4.26 by the stick antimony electrode. Another solution containing 2 ml. of c. p. lactic acid per 150 ml. was neutralized with sodium hydroxide to a pH of 3.68 as measured by the glass electrode. This solution by the antimony electrode gave a pH of 4.45. A solution of 5 grams of lactose in 150 ml. showed a pH of 5.86 by both the glass and antimony electrodes. These results indicate that the errors of the antimony electrode in dairy products are due to citrates and lactates.

Since citrate and lactate ions form complexes with antimony in solution, it seems probable that a similar complex formation takes place at the surface of the antimony electrode. As a result the electrode does not measure the true hydrogen-ion concentration of the solution.

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Routine High-Vacuum Distillation of Oils

An Apparatus and Conversion Chart

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A GENERALLY standardized method for evaluating the boiling points of heavy oils is badly needed for the extension of both the practical and scientific aspects of petroleum technology. In addition to the importance of the boiling range as an indication of volatility, it has been found (*5*) that most of the difficultly measurable physical properties of petroleum fractions are better correlated on the basis of boiling point than any other easily determined property.

Various types of equipment have been proposed for operation at pressures ranging from a few hundredths of a millimeter up to 10 or 20 mm. of mercury. The low pressures have the advantage of permitting the distillation of heavier stocks without decomposition. On the other hand, operation at low pressures increases the difficulty of manipulation and the uncertainty of converting the observed temperatures to normal boiling points at atmospheric pressure.

The apparatus here described was developed to permit operation at pressures of approximately 0.1 mm. of mercury. As compared to previously proposed methods, it has the advantage of satisfactory accuracy of pressure measurements, due to the elimination of condensable vapors in the McLeod gage. It is also unique in general design through the extensive use of ground-glass connections, which allows a minimum of difficulty in manipulation and cleaning. A new nomograph has also been devised for accurately converting observed temperatures to normal boiling points. As a result of the improved convenience of both the chart and apparatus, the method is satisfactory as a routine inspection and has been used as such for the past several months with gratifying consistency.

Davis and Hornberg (*4*) recently developed a vacuum distillation apparatus using a McLeod gage for accurate measurement of pressure. Outstanding features of this apparatus are the adequate size of the vapor delivery tube and the method of connecting the McLeod gage direct to the flask to avoid errors due to pressure drop in the delivery tube. However, in using an apparatus similar to that of Davis and Hornberg, it was found impossible to avoid errors due to diffusion of small amounts of condensable vapors into the McLeod gage. As a result the pressures read were appreciably too low, even though the amount of condensate formed was so small as to be invisible. Errors as great as 26.7° C. (80° F.) were encountered in the boiling points of pure compounds as determined in this way.

Errors due to condensation in the McLeod gage can be minimized by careful manipulation, although this procedure is both difficult and uncertain. A trap cooled with liquid air or solid carbon dioxide and placed in the line connecting the flask to the McLeod gage was found to eliminate all condensation in the gage. The amount of condensate collected in the trap never exceeds a few tenths of a cubic centimeter and introduces a negligible error in the distillation if suitable precautions are taken. The most important of these is flushing the entire McLeod gage and connecting lines with air before evacuating. The distilling flask is evacuated while the gage is filled with air at atmospheric pressure. The air in the gage is then slowly released into the flask before heat is applied, sweeping out all vapor and filling the connecting lines with air. Care is also taken to maintain a constant or diminishing pressure throughout the distillation.

Apparatus

The apparatus finally adopted is shown in Figure 1. Special attention was given to obtaining an arrangement easy to clean and reassemble. For this reason ground-glass joints were extensively used to minimize the difficulty of keeping the system vacuum-tight.

The distilling flask, *A*, is an ordinary round-bottomed flask of 300 cc. capacity to which is sealed the female portion of a 25-mm. interchangeable ground-glass joint. Several of these flasks may be prepared and used interchangeably. In the inside of the flask is a row of four sharp points directed downward toward the center, as shown. These points are made by heating a spot on the wall of the flask to redness and indenting it deeply with a small file. Although the flask is more difficult to clean, the points are of considerable value in puncturing the large liquid films that tend to rise up into the neck of the flask under many conditions of operation. With this arrangement it is ordinarily not necessary to use boiling chips or clay to prevent bumping and foaming.

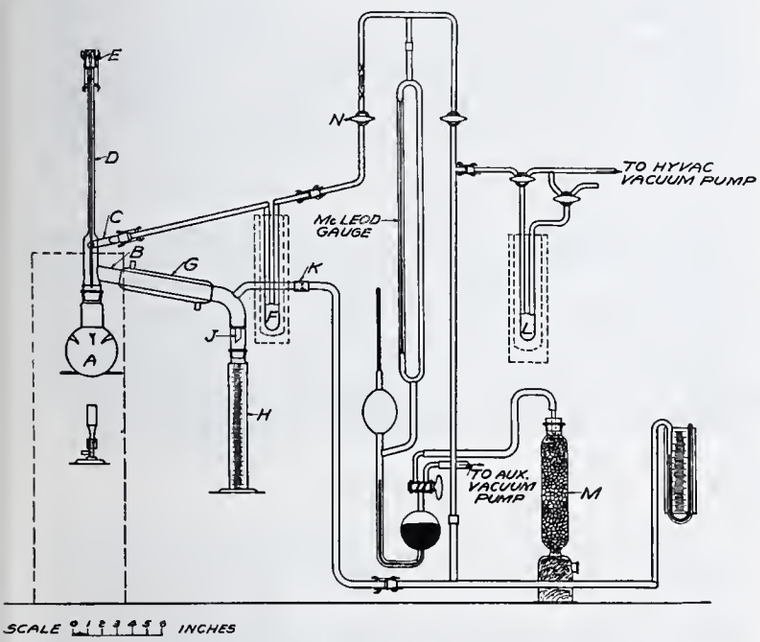

Figure 1. High-Vacuum Engler Distillation Apparatus

The male section of the interchangeable ground-glass joint is sealed to the vapor delivery tube, *B*, the McLeod gage connection, *C*, and the thermometer tube, *D*. The thermometer tube terminates in the male section of a ground-glass joint, *E*. The female section of the joint is sealed shut to form a cap and the thermometer suspended from a small glass hook sealed to the center.

The cooled condensate trap, *F*, is joined into the McLeod gage connection by two ground-glass joints. The trap itself is formed to fit loosely into a wide-mouth vacuum bottle of 450 cc. (1 pint) capacity. When distilling oils that contain no materials boiling below 205° to 260° C. (400° to 500° F.), this trap is satisfactorily cooled with acetone and solid carbon dioxide.

The vapor delivery tube is surrounded by a glass jacket, *G*, through which water is circulated, and which is sealed directly to the vapor tube. The end of the vapor delivery tube is curved downward, terminating in the male section of a ground-glass joint. The female section of this joint is sealed to a 100-cc. graduate, *H*. If desired, a dropping tip, *J*, may be sealed into the vapor tube above the graduate. This tip makes observation of the initial boiling point easy but complicates cleaning.

The vacuum pump line is connected to the vapor delivery tube by means of a short rubber tube connection, *K*. This one rubber tube connection is used to provide a certain amount of flexibility for assembly. The pump line is joined to the McLeod gage and to a manometer, as indicated. The pump is protected by a cooled trap, *L*, to condense any light materials which may pass through the condenser at the beginning of the run. This trap is ordinarily cooled with solid carbon dioxide and acetone only during the initial stages of evacuation. It is then by-passed by means of the two three-way stopcocks. It is not necessary to use this trap when running samples with initial boiling points above 232° C. (450° F.) if the water in the condenser is 15.6° C. (60° F.) or lower.

A good oil-sealed rotary pump is a satisfactory source of vacuum for work with oils boiling up to 537° C. (1000° F.). For operation of the McLeod gage an auxiliary vacuum pump of some type is necessary. A good water-jet filter pump will suffice. Dry air is admitted to the McLeod gage chamber through a calcium chloride drying tube, *M*.

A special compound manufactured by the Merco Nordstrom Valve Company (No. 650 for hot oils, gases, asphalt, and steam) was found satisfactory for lubricating the large ground-glass joint at the top of the flask. It is supplied in small sticks but tends to crumble to a powder. In applying it the joint is coated with a thin layer of ordinary high-vacuum stopcock grease and the powdered lubricant spread on this sticky surface.

Manipulation

Samples with low initial boiling points are topped in a preliminary distillation at atmospheric pressure to remove all material boiling below 260° C. (500° F.). In this procedure a charge of 200 cc. is weighed into a 250-cc. Engler distilling flask and distilled until the vapor temperature reaches 260° C. (500° F.). The amount of bottoms left in the flask is weighed and its specific gravity determined. The percentage bottoms by weight and by volume are calculated. The charge to the vacuum flask is then weighed out from the bottoms to correspond to exactly 100 cc. of the original sample. The vacuum distillation is recorded in volume units, adding the percentage volume overhead in the topping operation to the volumes of distillate recovered. If the sample has no extremely low-boiling material present and shows no noncondensable loss in the topping operation, the calculations may be simplified by topping out exactly a round figure volume percentage—for example, 10 or 20 per cent as indicated by the distillate collected.

In starting a distillation the McLeod gage is flashed with air and shut off from the rest of the system. The apparatus is then assembled and evacuated. If the sample contains low-boiling materials, trap *L* is cooled during the evacuation. When the pressure indicated by the manometer is less than 1 mm., stopcock *N* is opened, allowing the air in the McLeod gage to sweep out the connecting lines. Distillation is started when the pressure has reached a fairly steady value in the neighborhood of 0.1 to 0.3 mm. of mercury.

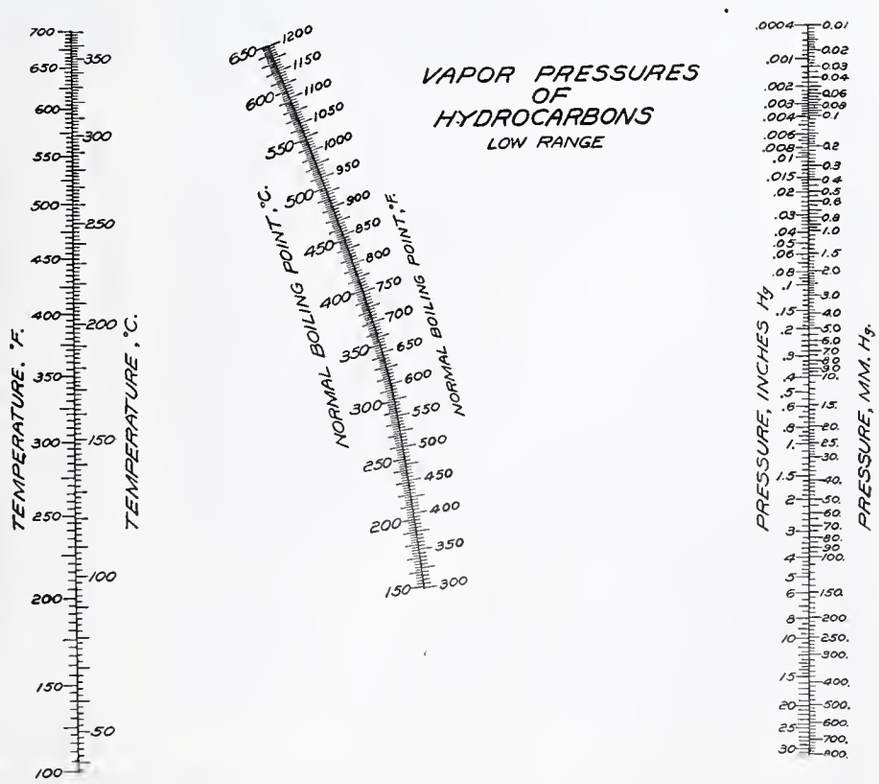

Figure 2. Boiling Point Conversion Chart

It has been found most satisfactory to operate at a distillation rate of 2 cc. per minute. Readings of temperature and pressure are recorded corresponding to each 5 cc. of distillate. Fortunately the distillation under high vacuum does not seem to be as sensitive to variations in operating conditions as the ordinary Engler distillation at atmospheric pressure.

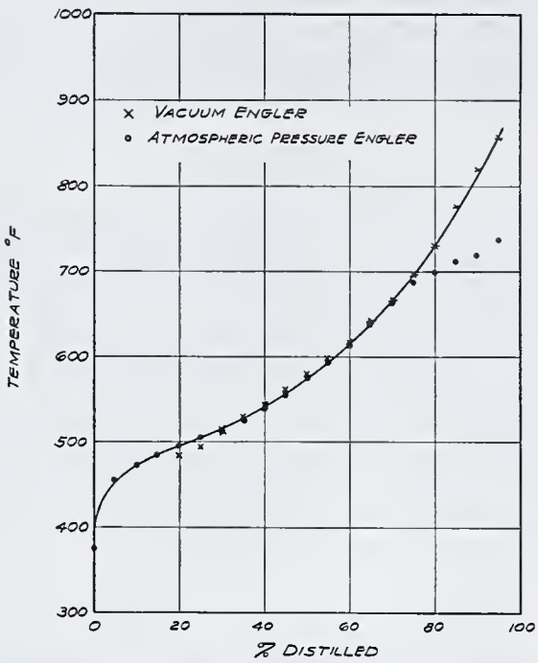

Figure 3. High-Vacuum and Atmospheric Engler Distillation Curves

Wide variation in distillation rate and size of flask caused little change in the results obtained. When operating in the range near 0.1 mm., pressure has no appreciable effect on the final results as long as cracking does not occur. Cracking is indicated by a sudden rise in pressure.

Temperature Conversion

The value of a high-vacuum distillation depends largely on the accuracy of the chart used for converting the observed temperatures to normal boiling points. Various equations and semi-empirical vapor-pressure charts have been proposed, most of which are unsatisfactory except over narrow ranges. The Cox chart (*3*) is one of the most extensively used, but its accuracy is not satisfactory where large pressure changes are involved. The vapor-pressure lines on the Cox chart are actually curved to a considerable degree, especially for high-boiling materials if the chart is laid out from the data on hexane.

Coats and Brown (*1*, *2*) have developed a method of correlating and extrapolating vapor-pressure data which, it is believed, is the most logical and reliable now available. Large-scale charts can be obtained from G. G. Brown at the University of Michigan, covering temperatures from −212° to 704° C. (−350° to +1300° F.) and pressures from 0.01 mm. of mercury to 5000 pounds per square inch. Where wide ranges of conditions are involved, it is recommended that this chart be used in preference to any of the other schemes which have been proposed.

The only disadvantage of the Brown and Coats chart is that it is somewhat difficult to read because of the wide range covered and the curvature of the pressure lines. For this reason the nomographic chart shown in Figure 2 was derived from the Brown and Coats chart to expedite routine conversions.

The pressure scale of Figure 2 was laid off proportional to the pressure intercepts on the 287.8° C. (550° F.) temperature line of the Brown and Coats chart. This gives a scale which is not logarithmic but gives considerable curvature when pressure is plotted against scale distance on semi-log paper. The deviation from logarithmic of the pressure scale derived in this way changes when different constant-temperature lines on the Brown and Coats chart are used as its basis. For this reason it is impossible to duplicate the entire Brown and Coats chart in nomographic or rectangular coördinates.

The temperature scale was derived by laying out a rectangular chart similar to that of Cox but using the empirical pressure scale described above. The temperature divisions were established by drawing a straight line on this chart at a 45° angle and designating it as representing the vapor pressure of the hydrocarbon boiling at 343.3° C. (650° F.). The temperature scale was then marked off from the Brown and Coats chart data for this boiling point. This resulted in a chart similar in appearance to the Cox chart but different in that both pressure and temperature scales are empirically derived.

Figure 2 was prepared by laying off the temperature and pressure scales directly from the rectangular coördinate chart described above. The boiling point scale was then established graphically, using the data of the Brown and Coats chart. The nomograph is in good agreement with this chart over the range of conditions encountered in ordinary vacuum distillations. Slight errors are introduced for extremely high- or low-boiling materials, but these errors are probably not greater than the error of the extrapolation to high temperatures in the original chart.

Results

In order to obtain the entire boiling range of a material having an initial boiling point below 260° C. (500° F.), it is necessary to run an ordinary 100-cc. Engler distillation at atmospheric pressure in conjunction with the vacuum distillation. The distillation is conducted in a 200-cc. flask using the A. S. T. M. condenser and burner shield, maintaining the distillation rate at 4 to 5 cc. per minute. The atmospheric pressure distillation is taken as correct for the lower part of the boiling range and the vacuum for the upper. The results given in Table I are typical.

Table I. Results of Distillation

Topping operation

	Sp. gr.	Grams	Cc.
Charge	0.9365	187.3	200
Bottoms	0.9446	151	160
Distillate	....	...	40
Loss			00

Vacuum distillation—charge, 75.5 grams

Distillate Cc.	Per Cent Over	Temperature °F.	Temperature °C.	Pressure Mm.	Normal Boiling Point °C.
0	20	150	65.6	0.35	251.7
5	25	154	67.8	0.31	257.2
10	30	164	73.3	0.28	268.3
15	35	174	78.9	0.265	276.1
20	40	184	84.4	0.240	285.0
25	45	194	90.0	0.220	294.4
30	50	204	95.6	0.180	304.4
35	55	214	101.1	0.155	314.4
40	60	225	107.2	0.135	323.9
45	65	240	115.6	0.105	338.9
50	70	252	122.2	0.085	350.0
55	75	277	136.1	0.084	363.3
60	80	310	154.4	0.105	387.8
65	85	346	174.4	0.095	412.8
70	90	390	198.9	0.120	437.8
75	95	426	218.9	0.160	457.8

Atmospheric pressure, 100-cc. Engler distillation

Distillate Cc.	Temperature °F.	Temperature °C.	Distillate Cc.	Temperature °F.	Temperature °C.
0	374	190.0	50	573	300.6
5	453	233.9	55	591	310.6
10	471	243.9	60	612	322.2
15	484	251.1	65	636	335.6
20	495	257.2	70	662	350.0
25	505	262.8	75	686	363.3
30	514	267.8	80	699	370.6
35	526	274.4	85	711	377.2
40	539	281.7	90	719	381.7
45	555	290.6	95	736	391.1

The two distillation curves are plotted in Figure 3. It will be noted that the lower portion of the vacuum distillation curve is in good agreement with that portion of the atmospheric pressure curve below cracking temperatures. This

close agreement is typical of the results on many different types of stocks and indicates that the method and conversion chart have a satisfactory degree of accuracy in this range. The final distillation curve is plotted by accepting the atmospheric pressure results in the low range and the vacuum in the high range.

The time required for a complete vacuum distillation, including assembling and cleaning the apparatus, ranges from 75 to 90 minutes. Additional time is required for the atmospheric pressure distillation and the topping operation if the sample contains light material.

ACKNOWLEDGMENT

The authors are indebted to R. A. Weppner and the analytical staff of the Universal Oil Products Company, particularly M. J. Stross, W. K. Simpson, and W. W. Johnstone, for valuable suggestions and assistance.

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Apparatus for Extraction of Solids by Upward Flow of Solvent

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IN PREPARING cottonseed meal for fat-free diets for small experimental animals, a larger apparatus than the usual Soxhlet extractor was required. Several difficulties that were encountered when this extraction was attempted in the apparatus ordinarily available were overcome by the use of the extractor illustrated in Figure 1.

It was found that when solvent was made to pass down through cottonseed meal, the meal tended to pack so that the flow of liquid through it almost stopped. However, when the flow of liquid was reversed, so that it was upward through the meal, the flow continued at a satisfactory rate indefinitely. Even with an upward flow of solvent, the meal caked enough to make its removal from the sides of a round vessel through a narrow aperture a tedious procedure. This objection was overcome in the present apparatus by making the walls straight from bottom to top with the opening at the top the full width of the cylinders. The inner cylinder containing the meal could be easily removed, and since the cylindrical form and wide top offered no obstruction, the cake could be shaken out in one mass.

An outside tube to conduct solvent from the condenser to the extraction chamber has the double disadvantage of being fragile and of cooling the solvent too much before it reaches the meal. The present apparatus was designed to avoid fragile projecting parts and to maintain a high temperature in the solvent where it is in contact with the meal. The wide space between the inner and outer cylinders for solvent returning from the condenser permits the free escape of gas bubbles, thus preventing the reduction of hydrostatic pressure on this side which might otherwise result from boiling of the solvent.

A surprisingly low head of liquid is required for upward flow of solvent.

It is considered desirable to stir the meal occasionally during extraction to break up any channeling that might have occurred. This was accomplished more easily in the cylindrical vessel than in a flask-shaped vessel.

CONSTRUCTION OF APPARATUS

The body of the extractor is constructed of Pyrex glass tubing. Since it is entirely separate, the inner cylinder may be constructed of either Pyrex or ordinary soda-lime tubing. The dimensions of the outside cylinder of the largest extractor used were approximately 6.25 × 55 cm. (2.5 × 22 inches). The center tube had an inside diameter of about 10 mm. The limits of the size of this tube are determined on the one hand by the undesirability of sacrificing more space than necessary, and on the other hand by the requirement that the tube allow free passage of vapor and extract in opposite directions. The space between the inside and outside cylinders was about 2 mm. Provision for connection with the boiling flask may be by a plain tube and cork or by a standard-taper glass joint.

The condenser is made of thin copper sheeting by soldering a plain cone to one end of a short cylinder and a disk to the other. The diameter at the base of the cone is such that a clearance of about 0.5 mm. is left between the edge of the cone and the inside wall of the outer glass cylinder. The function of the projecting edge of the cone is to direct solvent against this wall so that it flows into the space between the inner and outer cylinders. The disk which forms the top of the condenser is made large enough to extend well over the top edge of the extractor. Copper inlet and outlet tubes for cooling water are soldered in place.

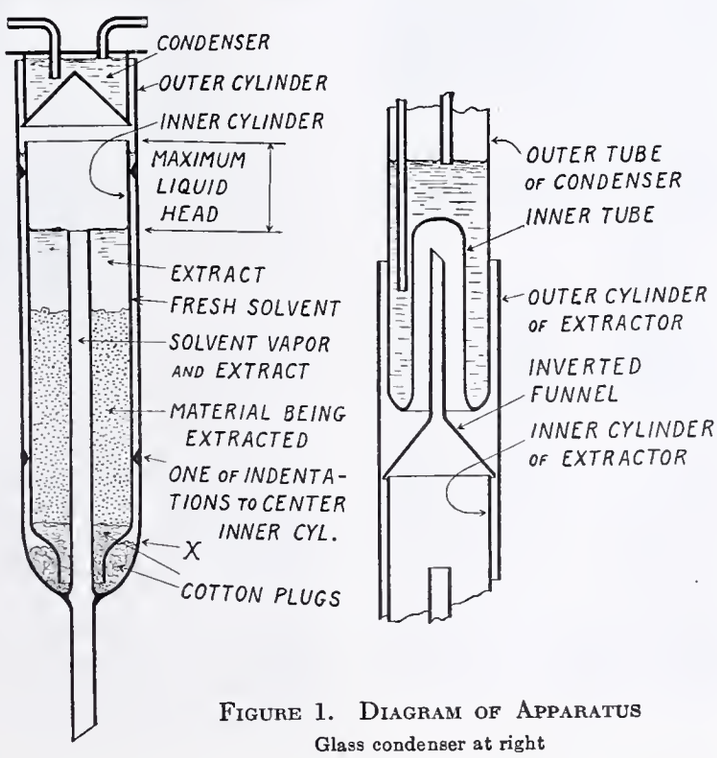

FIGURE 1. DIAGRAM OF APPARATUS
Glass condenser at right

If possible contamination with copper were objectionable, the condenser could be made of some other metal or of glass. A form of glass condenser which was tried is shown on the right (Figure 1). A thin-walled tube, closed at one end, is fused at its open end to the bottom of a larger tube, which should have as thin walls as is consistent with the desired mechanical strength. An ordinary funnel inverted over the top of the inner cylinder completes this set-up, the stem conducting the vapor into the inner tube of the condenser and the funnel itself diverting the returning solvent to the space between the two cylinders of the extractor. The condenser is supported by a clamp, and is provided with cooling water tubes through a stopper. Although the glass condenser functions fairly well, a metal one is more satisfactory where permissible. Because of the more rapid transfer of heat, the metal condenser may be made shorter, thereby avoiding undesirable length in the outer cylinder.

Before filling the extractor, cotton is placed in the bottom of the outer cylinder to act both as a filter and as a cushion for the inner cylinder. More cotton may be placed in the bottom of the inner cylinder after it is in place, if desired, to distribute the solvent better through the meal. During filling, the center tube may be protected by a cork or cotton plug or by a short piece from the bottom of a test tube.

The weight of the inner cylinder and its contents compresses the cotton filter and adds unnecessarily to the head required to maintain a flow of solvent. There are several ways of eliminating this resistance to flow: small holes may be made in the inner cylinder as near as possible to its bottom edge; washed and ignited sand may be placed in the bottom of the outer cylinder before the cotton is put in; or the inner cylinder may rest on indentations made in the outer cylinder (X, Figure 1) instead of on the cotton.

The depth of material to be extracted is governed mostly by the depth of solvent required above it for settling of the finer particles of the solid. If necessary, when there is an interest in the extract as well as in obtaining fat-free meal, a cotton plug may be placed above the solid material being extracted, to act as a filter.

Since the maximum obtainable head of liquid is fixed by the difference in level between the top of the solvent vapor tube and the top of the inner cylinder, it may sometimes be necessary to reduce the depth of the material being extracted to insure adequate flow of solvent. However, this difficulty has not been encountered in the extractions attempted. A head of 10 cm. (4 inches) gave ample margin for the extraction of about 20 cm. (8 inches) of cottonseed meal.

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A Rapid Method for Making Standard Solutions of Specified Normality

Otto Johnson

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CONSIDERABLE loss of time may be averted in the preparation of standard solutions of exactly specified normality by the use of the method outlined below.

Example: Prepare 18 liters of an 0.1142 N solution of sulfuric acid:

1. Calculate its equivalent in terms of a normal solution: $18 \times 0.1142 = 2055.6$ ml. of normal solution.
2. Prepare about 1100 ml. of an approximately 2 N solution of sulfuric acid. From (1) it is evident that about 1028 ml. of this solution are equivalent to 18 liters of 0.1142 N solution.
3. Into approximately 17 liters of water measure accurately about 1000 ml. of the 2 N acid, so that the standard solution is less than the desired normality. If the normality is greater than the desired value, dilute with water but do not discard any solution.
4. Determine the normality of the above solution. For purposes of illustration assume that it is found to be 0.1109 N.
5. From these data it is possible to calculate exactly the number of milliliters of the 2 N solution required for this volume of standard solution by means of the equation

$$1000:x::0.1109:0.1142$$

from which $x = 1030$. This represents the total number of milliliters of 2 N solution required to make the standard solution exactly 0.1142 N and when the additional 30 ml. of 2 N solution are added the final determination of normality may be made.

This procedure will be found less laborious than the customary one of making the solution stronger than desired and then diluting with water. The accuracy depends upon the care with which the first determination of normality is carried out, since 1 ml. of the 2 N acid makes a difference of only slightly more than one in the fourth place in the particular example cited. When the work is done carefully the final determination of normality need serve only as a check and rigorous adherence to this procedure will be found to result in an economy of both time and effort.

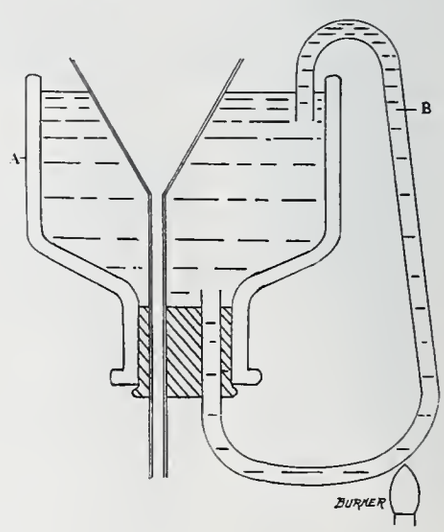
Received September 22, 1934.

A Hot-Water Funnel

John R. Caldwell

Ohio State University, Columbus, Ohio

THE sketch shows the design of an easily constructed hot-water funnel. The container, A, is made by cutting the top from a bottle of convenient size. The side tube, B, may be constructed of glass or copper tubing, and should be 8 to 10 mm. in diameter to insure rapid circulation. The model shown is designed for heating with a Bunsen burner, but a resistance coil may be wound on the side tube for electrical heating.



The design is easily adapted to any size, and lends itself readily for use in semi-microwork where very small apparatus is essential. Büchner funnels as well as the 60° glass funnels may be accommodated. A few grams of salt dissolved in the water will raise the temperature of the bath so that, when aqueous solutions are filtered, they are maintained at the boiling point. It is recommended that the rubber stopper be wired in place.

Received October 17, 1934.

Rapid Method for Quantitative Determination of Carbon in Organic Compounds

C. B. Pollard and W. T. Forsee, Jr., University of Florida, Gainesville, Fla.

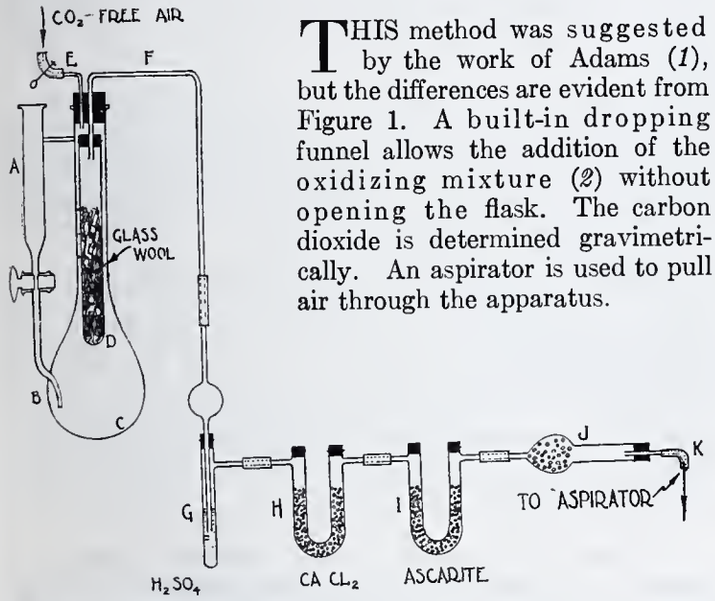


Figure 1. Diagram of Apparatus

This method was suggested by the work of Adams (*1*), but the differences are evident from Figure 1. A built-in dropping funnel allows the addition of the oxidizing mixture (*2*) without opening the flask. The carbon dioxide is determined gravimetrically. An aspirator is used to pull air through the apparatus.

The procedure is similar to that of any other wet oxidation. Before admitting the oxidizing mixture, disconnect the aspirator and close the intake at *E*. Pour 10 cc. of the oxidizing solution into the dropping funnel, *A*, and admit this into the flask. (Keep the stem of the funnel full of liquid at all times during the determination.) Immediately admit 30 to 50 cc. of the acid mixture. Heat the flask with a very small flame (about 1.25 cm. high). In some cases oxidation will proceed immediately without heating. The amount of heating must be gaged by the rate of oxidation of the sample. After the oxidation becomes slow, connect the aspirator, increase the heating, and allow air to pass through from 1 to 2 hours. This length of time has been found ample for all compounds used and in most cases this was shortened a great deal, depending upon the rapidity of oxidation. For cooling the flask neck, a slow stream of compressed air may be directed upon it. This will allow more rapid heating and thus shorten the time required for complete oxidation.

Satisfactory and consistent checks with the theoretical percentage of carbon have been obtained when using various types of organic compounds. The results of a few of the carbon determinations by this method are shown in Table I. This method has been satisfactorily used in these laboratories for the past 2 years by students of quantitative organic analysis and in organic research.

Table I. Analyses of Compounds

Substance Analyzed	Carbon Found	Theoretical Carbon	Difference
	%	%	
Cerium phenylacetate	51.19	51.22	0.03
Thiocarbanilide	68.35	68.36	0.01
p-Nitrobenzoic acid	50.29	50.29	0.00
Diazoaminobenzene	73.02	73.05	0.03
Piperazoniumphenylacetate	66.98	67.00	0.02
Oxalic acid	19.00	19.04	0.04

Acknowledgment

The authors express their appreciation to J. E. Adams and R. M. Barnette for valuable suggestions.

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Effect of Asparagine on the Reducing Power of Levulose

Ione Weber, Edna J. Posen, and Nedda G. Ceboolsky, Brooklyn College, Brooklyn, N. Y.

A study of the effects of nitrogen compounds on the determination of sugars by copper reduction methods has been undertaken. Nitrogen compounds, principally asparagine and aspartic and glutamic acid, are present in raw sugar sirups. Non-glucose-reducing substances are present in blood and urine. The determinations reported in Table I are on levulose in the presence of asparagine.

Levulose supplied by the Bureau of Standards and Eimer and Amend asparagine c. p. were used. The volumetric method of Jackson (*1*), modified to the extent of evaporating the nitric acid solution of cuprous oxide almost to dryness and dissolving the residue in water, was used for most of the determinations. The result reported in each case is the average of two to four determinations.

The difference between the result for asparagine plus levulose and the result for levulose alone in each case is within the experimental error.

The proportion of asparagine to levulose in the above experiments is very much greater than the proportion in blackstrap (commercial raw sirup). The conclusion can be drawn that the presence of asparagine does not affect the determination of levulose by the Nijns method at 49° C.

Table I. Effect of Asparagine

Sugar	Asparagine	Copper Average	Deviation from Sugar Blank	Deviation of Analysts
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
20	0	65.3	...	2.7
20	12	65.1	0.2	1.9
20	15	67.6	2.3	1.4
20	18	65.4	0.1	1.8
0	18	1.0	...	...
35	0	114.0	...	0.6
35	8	112.9	1.1	2.6
35	10	111.9	2.1	3.5
35	12	110.3	3.7	1.8
0	10	0.5	...	...
35	0	112.1[a]	...	7.5
35	8	110.7[a]	1.4	8.7
35	10	109.0[a]	3.1	5.2
35	12	109.1[a]	3.0	8.5
0	10	1.4[a]	...	...
50	0	163.1	...	3.8
50	12	162.1	1.0	3.6
50	15	162.1	1.0	1.0
50	18	162.6	0.5	2.9

[a] Results obtained by the gravimetric method using Nijns solution (*2*).

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Received June 16, 1934.

Roulette Comparator for Colorimetric Analysis

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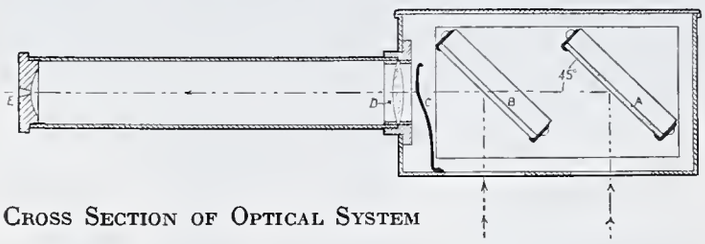
THE roulette comparator is designed to assist in securing a precise matching of colored solutions in Nessler tubes. A revolving circular rack carries a series of ten standard solutions in 100-ml. Nessler tubes. Beside this is a stationary rack which holds the tube containing the unknown solution. A rachet device on the circular rack allows the standard tubes to be brought, one by one, into a fixed position beside the tube containing the solution to be matched. Below the tube containing the unknown and the standard tube in fixed position beside it is an adjustable light-reflector, having a mirror on one side and white glass on the reverse side. The white glass is ground to a plane, matte surface. The source of light may be either skylight (preferably north sky) or a daylight colorimeter lamp. The white glass reflector is generally used for matching lightly colored solutions where a low intensity is desired and the mirror for darkly colored solutions where the light intensity must be greater.



Cross Section of Optical System

Light from the reflector passes up through the two tubes under comparison, impinges on mirrors *A* and *B*, and is reflected horizontally through the observation tube. One-half of the circular field of light from the right-hand Nessler tube is cut off by mirror *B*, the edge of which thus serves as a dividing line between the two halves of the circular field. The image of one-half of the right-hand tube is then observed in juxtaposition to the opposite half of the image of the left-hand tube. The observation tube is provided with an eyepiece, *E*, having a hole 1.5 mm. in diameter and at the end next to the mirror box is a diaphragm having an aperture 24 mm. in diameter. By having the apertures of the eyepiece and diaphragm properly proportioned, only the image of the bottoms of the Nessler tubes can be seen, thus preventing interference by light reflected from the inner sides of the tubes.

A magnifying lens *D* is placed in the light path between the mirrors and the eyepiece. This enlarges the circular image and permits a better matching of the two half-fields. Upon looking through the eyepiece, the observer sees a large circular field, divided by an almost imperceptible line when the light from the two solutions has the same intensity. The mirror box and observation tube are painted dull black inside.

Two metal spring clips whose position is indicated by *C* are placed in the mirror compartment, between the mirrors and the lens, to permit the use of color filters. The mirror box is so attached that it can be rotated through 180° to permit a check on the adjustment of the mirrors and on the matching, and also to allow observations in case fumes from the solutions are objectionable. The Nessler tubes (100-ml. low form) have double-plane, fused-on bottoms instead of being ground on the outside only as were the old type bottoms. This is a decided improvement, since a uniform field of the same degree of color intensity is obtained.

A further use of the apparatus is possible in case it is desired to compare the spectra of two solutions. The eyepiece, *E*, is threaded so that it can be removed, and by means of a fairly short focus lens an image of the two half-fields can be formed on the slit (placed horizontally) of a spectroscope. This arrangement also permits photographing the two spectra side by side on one film.

Acknowledgment

The authors wish to express their thanks to the American Instrument Company, Washington, D. C., for building the roulette comparator.

Received December 6, 1934.

Determination of the Phosphorus Fractions in Blood Serum

R. R. Roepke, Kansas Agricultural Experiment Station, Manhattan, Kans.

IN OVERCOMING the difficulty of proper pH control in determining phosphorus by the colorimetric method, Green (*1*) ashed the sample with calcium acetate and finally neutralized with ammonium hydroxide using phenolphthalein as indicator before developing the color, a procedure which does not give satisfactory results. This procedure has the disadvantage also that the ash contains some carbon particles even with careful heating. The following procedure eliminates these difficulties:

Total Phosphorus. Into a 150-cc. beaker, pipet an aliquot of diluted serum containing from 0.05 to 0.15 mg. of phosphorus. Add 2 cc. of magnesium nitrate (50 per cent solution of $Mg(NO_3)_2 \cdot 6H_2O$) and evaporate on hot plate, increasing the heat until a portion of the ash has become white. Fifteen to twenty minutes at the highest temperature are sufficient. If a portion of the ash has become charred, it will be necessary to add several cubic centimeters of water and a drop of nitric acid and repeat the heating.

When dry, heat the sample over a free flame (or in a muffle) until all the magnesium nitrate has been decomposed. This should leave a white ash. Dissolve the ash in 2.5 cc. of 10 *N* sulfuric acid and 10 to 20 cc. of water, heating to insure complete solution. Cool, add a piece of Congo red test paper, and neutralize with ammonium hydroxide. Transfer the solution to a 100-cc. volumetric flask through a small funnel containing a bead or some other form of constriction which will retain the test paper. Add sufficient water to bring the volume to 70 or 80 cc. Prepare standard by adding 5 to 15 cc. of standard phosphorus solution (0.01 mg. of phosphorus per cc.) and 5 cc. of 5 *N* ammonium sulfate to a 100-cc. volumetric flask and dilute to 70 to 80 cc. To both add from a buret 2 cc. of molybdic sulfuric acid reagent (Denigès reagent). Dilute to the mark, add 0.5 cc. of the stannous chloride solution, and mix. After 1 or 2 minutes compare in a colorimeter, setting the standard at 30. The unknown should read within 3 or 4 units of the standard.

Lipoid Phosphorus. Transfer 10 to 20 cc. of the alcohol-ether filtrate (corresponding to 0.2 to 0.4 cc. of serum) to a beaker containing 1 cc. of magnesium nitrate and proceed as for total phosphorus.

Total Acid-Soluble Phosphorus. Transfer 5 to 10 cc. of trichloroacetic acid filtrate (1 volume of serum to 4 volumes of 10 per cent trichloroacetic acid) and 1 cc. of magnesium nitrate to a beaker and proceed as for total phosphorus. Care should be taken to see that all the trichloroacetic acid has been volatilized by heating on the hot plate before heating over a free flame, since too rapid heating will cause it to char.

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Calcium Hypochlorite as a Volumetric Oxidizing Agent

Stability and Standardization of the Solution. Determination of Ammonia

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Solutions of hypochlorite have found little application in volumetric analysis since in general they have been found unstable. It was found that "H. T. H" calcium hypochlorite yielded solutions which were quite stable. By adding an excess of bromide to the sample to be titrated, the added hypochlorite behaves as hypobromite. A systematic study is being made of the application of standard hypochlorite to the determination of various reducing substances. In this paper the standardization of the solution either in acid or weakly alkaline medium, with Bordeaux as indicator, is described and its use in the determination of ammonia investigated.

IT HAS come to the authors' attention that "H. T. H.," a calcium hypochlorite of high available oxidizing strength manufactured by the Mathieson Alkali Works, New York, yields stable solutions. This being the case, they have attempted to make use of the product in the quantitative oxidation of various reducing substances. In general, hypobromite acts more rapidly in oxidations than does hypochlorite, but is much less stable. Since hypochlorite reacts quickly with bromide to form hypobromite, the advantages of both stability and rapid oxidation may be obtained by keeping a stock solution of calcium hypochlorite and adding an excess of alkali bromide to each sample before titration. By this means calcium hypochlorite may be expected to become useful in any reaction at present involving the use of sodium hypobromite or bromine-bromide solutions. (It may be mentioned that K. Jellinek and W. Krestoff, *4*, used sodium hypochlorite as a standard reagent. They kept the stock solution in clear glass bottles and found after 17 days of standing a decrease in strength of about 2 per cent. Possibly the reagent would have been found more stable if protected from light.) The authors are now engaged in a study of the application of calcium hypochlorite to the determination of various inorganic compounds; and it should be useful as well in quantitative organic analysis. In this paper are discussed the stability and other general properties of calcium hypochlorite solutions, indicators for use in weakly alkaline and acid media, and an application to the determination of ammonia. Subsequent papers will deal with the determination of several other inorganic substances.

REAGENTS

CALCIUM HYPOCHLORITE. The solid "H. T. H." was obtained from the Mathieson Alkali Works in cans, but as these after opening soon became corroded, the material was transferred to glass-stoppered bottles. The solid is not stable, losing strength gradually whether or not it is exposed to light. J. J. Lingane, of this laboratory, has analyzed a sample of uncertain age, probably over 4 years, with the following results expressed in percentages: moisture, 2.10; available chlorine (as OCl^-), 31.5 (active chlorine, 43.4); total chlorine, 45.5; total calcium as Ca, 22.36; Na, 10.59; Fe_2O_3, 0.54; free CaO, 3.17; $CaCO_3$, 6.08. The fresh product contains about 60 per cent of available chlorine.

To prepare approximately 0.1 *N* solutions, about 16 grams of the solid are taken for 2 liters. It was found convenient to stir the solid into about 500 cc. of water, allow to settle, and filter through paper in a Büchner funnel, then dilute the filtrate to about 2 liters and refilter if necessary. Calcium carbonate which may appear as a turbidity is not harmful, but soils burets rather quickly. The solution is preferably kept in a bottle painted black on the outside, or at least protected from light as much as possible. A reagent prepared in the foregoing manner upon analysis was found to be equivalent to a solution 0.0267 *M* in calcium hypochlorite (0.1068 *N* oxidizing strength), 0.0019 *M* in calcium hydroxide, 0.0086 *M* in calcium chloride, and 0.0306 *M* in sodium chloride. The ratio of sodium to calcium is variable in different solutions, as varying amounts of calcium are removed in filtration.

SODIUM ARSENITE. Pure arsenious oxide from the Bureau of Standards was dissolved to make 0.1000 *N* sodium arsenite solutions according to the directions of Kolthoff (*5*), and 0.0100 *N* solutions were prepared by appropriate dilution.

INDICATORS. G. F. Smith of the University of Illinois kindly furnished samples of the indicators studied by himself and Bliss (*10*) for use in bromate titrations. These and various other indicators were used without further purification, in 0.2 per cent aqueous solutions to which equivalent amounts of sodium hydroxide were added if necessary.

AMMONIUM COMPOUNDS. Determinations of ammonia were made using stock solutions of ammonium hydroxide or ammonium chloride. The former were prepared from redistilled ammonia and were kept free from carbon dioxide, being standardized acidimetrically. The latter were prepared from carefully dried C. P. ammonium chloride.

The other salts used, potassium bromide and the buffering

agents, were C. P. quality, recrystallized if necessary. The potassium bromide should not contain over 0.01 per cent of iodide, as this is oxidized to iodate by hypobromite, thus causing an error if the solution is not subsequently acidified. Conductivity water was used in all experiments.

Standardization of Calcium Hypochlorite Solutions

The standardization may be made either of several ways, corresponding to various methods which may be followed in actual determinations. With use of hypochlorite for direct titrations in acid solution, any of the nonreversible indicators used in bromate titrations of sodium arsenite are satisfactory, provided an excess of bromide is present. For use in indirect determinations, the hypochlorite is best standardized by pipetting a known volume into excess potassium iodide, acidifying with 10 cc. of 4 N sulfuric acid, and titrating with standard sodium thiosulfate to the disappearance of the blue color with starch.

It is a particular advantage of hypochlorite that determinations may be made entirely in basic solutions, thus eliminating interference of many oxidizing agents such as chromate, iodate, and bromate. The procedure for standardization is simple, and the same whether direct or indirect titrations are involved in the determinations.

To 25 cc. of standard sodium arsenite in a 200-cc. Erlenmeyer flask add 10 cc. of a solution containing 10 per cent potassium bromide and 5 per cent sodium bicarbonate. Titrate at a moderate speed with hypochlorite until near the expected end point, add 0.05 cc. of a 0.2 per cent solution of Bordeaux, and titrate dropwise with thorough stirring until the color fades. Then add another 0.05 cc. of indicator and, if it does not fade, add more hypochlorite cautiously until a split drop causes the solution almost to "flash" from pink to colorless or light yellow-green. Since these indicator reactions are not reversible, one must make certain that the end point has actually been reached when the color has faded; this should be tested by the addition of more indicator. It is advantageous to use as little indicator as possible and, when the approximate end point is known, one can perceive the end point sharply with only one or two drops. The total amount used should be known and the indicator correction made on the basis of the results below.

The standardization may also be made potentiometrically against arsenite in bicarbonate medium, using a bright platinum electrode, agar–potassium chloride salt bridge, and calomel half-cell. A sharp rise in potential appears in close agreement with the end point obtained with Bordeaux indicator.

Indicators and Corrections

As mentioned above, any of the common bromination indicators may be used with hypochlorite in acid bromide solution. Bordeaux serves very well; 0.10 cc. of 0.2 per cent Bordeaux solution requires 0.012 cc. of 0.1 N hypochlorite for decoloration, good proportionality holding for other amounts regardless of moderate change in dilution.

For use in weakly alkaline solutions containing bromide the indicators given in Table I have been chosen, largely from the list studied by Smith and Bliss (*10*).

Table I. Indicators for Weakly Alkaline Media

Indicator	British Colour Index No.	Color Change
Bordeaux	88	Pink ⟶ very faint yellow-green
Brilliant Ponceau 5 R	185	Pink ⟶ colorless
Naphthol blue black	246	Blue ⟶ violet-pink ⟶ colorless
Congo Corinth	375	Pink ⟶ light yellow
Indigo carmine	1180	Blue ⟶ green ⟶ light yellow

Bordeaux is recommended most highly. For titrations in solutions containing 0.5 to 1.0 gram of potassium bromide and 0.5 gram of either sodium bicarbonate, disodium phosphate, or sodium carbonate, the indicator correction for Bordeaux is approximately 0.02 cc. of 0.1 N hypochlorite for each 0.10 cc. of 0.2 per cent indicator, plus a constant amount of 0.01 cc. if the total volume is 50 cc. or 0.02 cc. if the volume is 100 cc.

Nearly all of the common pH indicators as well as several dyes have been investigated, but all except the above have been rejected as bromination indicators since they react either too rapidly or too slowly with hypobromite in alkaline solution. None of the common reversible oxidation indicators have been found useful under the conditions employed. In any case the indicator must be used in aqueous rather than alcoholic solution.

Stability of Calcium Hypochlorite Solutions

Experiments have shown that the stability of calcium hypochlorite solutions decreases with decreasing concentration of the solutions, with exposure to light, and with frequent opening of the containers. Chapin (*2*) found that potassium hypochlorite has its maximum stability at a pH of 13.1. The 0.1 N solutions employed by the authors probably have a pH between 11 and 12. In general, calcium hypochlorite solutions are more stable than sodium hypochlorite and far more stable than hypobromite. The results in Table II show the stability that may be expected when approximately 0.1 N and 0.01 N solutions of "H. T. H." are kept in glass-stoppered bottles painted black on the outside, at an average temperature of 25° C. with occasional variations of ± 5° C. A 0.01 N solution exposed to average room light lost 9 per cent of its strength in 2 days.

Table II. Stability of Calcium Hypochlorite Solutions

Time after Preparation		Approximately 0.1 N Solutions			Approximately 0.01 N Solutions	
Months	*Days*					
..	1	0.1262	....	0.0895	0.00919	0.00918[a]
..	5	....	0.1047	....	.....	.....
..	15	....	0.1044	....	.....	.....
1	..	....	0.1042	....	.....	.....
1	15	....	0.1041	....	0.00905	0.00905
2	..	....	0.1040	....	.....	.....
3	..	0.1258	....	0.0884	.....	.....
4	15	....	....	....	0.00880	.....
6	..	....	0.1035	0.0881	.....	0.00893
8	19	....	....	....	0.00822[b]	.....
8	20	....	....	....	0.00820[b]	.....
8	26	....	....	....	0.00814[b]	.....
9	3	....	....	....	0.00808[b]	.....
15	..	0.1230	....	....	.....	.....
16	..	0.1230	....	....	.....	.....
24	..	....	....	....	0.00535	.....

[a] This solution contained a larger excess of calcium hydroxide than the other and appeared to be more stable.
[b] Determination made by E. B. Sandell.

Table III. Iodometric Determination of Ammonia

Nitrogen Taken	Buffer	Time of Standing	Nitrogen Found	Error
Mg.	*Gram*	*Min.*	*Mg.*	%
14.01	0.5 $NaHCO_3$	1	13.96	−0.4
14.01	0.5 $NaHCO_3$	15	14.02	+0.1
14.01	0.5 $NaHCO_3$	5	14.01	0
14.01	0.5 $NaHCO_3$	5	14.04	+0.2[a]
14.01	1.0 Na_2HPO_4	5	14.02	+0.1
14.01	1.0 $Na_2B_4O_7.10H_2O$	5	14.05	+0.3[b]
14.01	1.0 $NaOAc.3H_2O$	5	14.14	+0.9
0.700	0.5 $NaHCO_3$	5	0.710	+1.4

[a] In presence of 30 mg. KNO_3.
[b] Return of starch color after end point indicated nitrite formation.

Application to Determination of Ammonia

The iodometric determination of ammonia has been investigated thoroughly by several groups of workers (*1, 3, 6, 7, 8, 9, 11*), the general conclusion being that the oxidation of ammonia to nitrogen and water

$$2NH_3 + 3OBr^- \longrightarrow N_2 + 3H_2O + 3Br^-$$

takes place quantitatively in excess hypobromite at a pH close to 8. The authors have obtained good results using hypochlorite instead of hypobromite as standard solution, by first adding an excess of potassium bromide to the weakly alkaline ammonia solution. The mixture is allowed to stand 3 to 5 minutes with a slight excess of hypochlorite, then treated with potassium iodide and acid, and back-titrated

with standard thiosulfate. Table III shows the effect of varying conditions, 1.0 gram of potassium bromide having been used throughout.

Teorell (*11*) has introduced a sensitive micromethod for ammonia, back-titrating the excess hypobromite with naphthyl red. It seems probable that calcium hypochlorite could profitably be substituted in this method as well, being more stable than the sodium hypobromite originally specified.

Table IV. Determination of Ammonia in Alkaline Medium

Nitrogen Taken	Buffer	Time of Standing	Nitrogen Found	Error	Salts Present
Mg.	*Grams*	*Min.*	*Mg.*	%	*Mg.*
10.51	5 $NaHCO_3$	3	10.61	+1.0	...
10.51	3 $NaHCO_3$	3	10.55	+0.4	...
10.51	1 $NaHCO_3$	3	10.51	0.0	...
10.51	1 $NaHCO_3$	12	10.52	+0.1	...
14.01	0.5 $NaHCO_3$	15	14.06	+0.4	...
14.01	0.5 $NaHCO_3$	5	14.04	+0.2	...
14.01	0.5 $NaHCO_3$	5	14.05	+0.3	30 KNO_3
14.01	1 $Na_2B_4O_7.10H_2O$	5	14.12	+0.8	...
14.01	1 $NaOAc.3H_2O$	5	14.22	+1.6	...
14.01	1 Na_2HPO_4	5	14.03	+0.2	...
14.01	1 Na_2HPO_4	3	14.00	−0.1	27 $CuCl_2$
14.01	1 Na_2HPO_4	3	14.02	+0.1	32 $FeCl_3$
14.01	1 Na_2HPO_4	3	14.01	0.0	28 $KBrO_3$
14.01	1 Na_2HPO_4	3	14.01	0.0	10 $K_2Cr_2O_7$

Oxidizing substances interfere with the iodometric method. Therefore, a procedure in which the solution could be kept alkaline throughout would be of advantage, since the interfering action of various oxidizing agents could then be avoided. Accordingly, the authors attempted the direct titration of ammonia with hypochlorite using excess bromide and Bordeaux as indicator, but the reaction was found too slow and the indicator faded prematurely. By first adding excess hypochlorite, and then a known excess of arsenite, the titration could be completed with Bordeaux as indicator just as in the standardization of hypochlorite against arsenite. The authors have adopted the following procedure, in which 0.1 *N* hypochlorite is used for samples containing 5 to 25 mg. of nitrogen and 0.01 *N* hypochlorite for smaller amounts:

To about 25 cc. of the nearly neutral ammonia solution in an Erlenmeyer flask add 10 cc. of a solution 10 per cent in potassium bromide and 5 per cent in sodium bicarbonate, and titrate with hypochlorite until a permanent light yellow color appears, indicating a slight excess. Allow to stand 3 to 5 minutes, then add from a pipet 10 cc. of 0.01 *N* sodium arsenite. Shake well and add 0.05 cc. of 0.2 per cent Bordeaux, which should impart a pink color to the solution. If the color fades, more arsenite and indicator should be added. Continue the titration with hypochlorite to the end point as in the standardization against arsenite. Calculate the amount of hypochlorite corresponding to the arsenite and indicator added, and deduct this from the total volume used. The difference represents the amount of ammonia oxidized on the basis of three equivalents of hypochlorite per mole of ammonia. (1.0 cc. of 0.10 *N* hypochlorite corresponds to 0.467 mg. of ammonia nitrogen.)

The results in Table IV show the accuracy of the method under various conditions. Evidently the oxidizing agents added did not interfere. Disodium phosphate instead of sodium bicarbonate was used in the presence of iron and copper, since the color became less troublesome. More than 10 mg. of potassium dichromate rendered the indicator change indistinct. The potentiometric method (back-titration of the excess arsenite with standard hypochlorite solution) yielded excellent results and is especially advantageous in the presence of colored compounds or in the determination of extremely small amounts of ammonia with reagents 0.01 *N* or even more dilute.

The data in Table V show that quantities of ammonia as small as 0.5 mg. in a volume of 25 cc. can be determined with a maximum error of about 2 per cent, using the general procedure described above. The iodometric procedure yields errors of the same magnitude but is preferable in the absence of other oxidizing substances, since the color change of the iodine starch is sharper than that of Bordeaux in these very dilute solutions. Blanks should be run along with the determinations, as traces of reducing substances are likely to be present in the water used as a solvent and some bromine or oxygen may be lost by decomposition of the hypobromite on longer standing.

Table V. Determination of Small Amounts of Ammonia

Nitrogen Taken	KBr	$NaHCO_3$	Time of Standing	Nitrogen Found	Error
Mg.	*Grams*	*Grams*	*Min.*	*Mg.*	%
1.050	1	1	5	1.071	+2.0
1.050	1	1	3	1.068	+1.7
1.050	1	1	15	1.077	+2.6
1.050	1	3	3	1.068	+1.7
1.050	1	3	15	1.074	+2.3
1.050	3	1	3	1.057	+0.7
1.050	3	1	8	1.059	+0.9
0.700	1	0.5	5	0.711	+1.6
0.420	1	1	3	0.419	−0.2

Conclusions

Solutions of "H. T. H." calcium hypochlorite are quite stable if kept in the dark and are recommended as standard solutions in volumetric analysis.

Hypobromite oxidizes more rapidly than hypochlorite; the former is obtained from the latter by adding an excess of alkali bromide.

Hypochlorite may be standardized against arsenic trioxide using Bordeaux as indicator, in acid or weakly alkaline solution.

Procedures have been given for the determination of quantities of ammonia from 0.5 to 20 mg.

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Opacity Standards for Paper Testing. The development of glass standards for the calibration of instruments used to test the opacity of paper by the contrast ratio method, as specified in the standard method of the Technical Association of the Pulp and Paper Industry, is described by Deane B. Judd in the September issue of the Bureau of Standards Journal of Research.

According to this method the reflectance of the material backed by a perfectly absorbing surface divided by its reflectance when backed by a highly reflecting material such as magnesium oxide is taken as an index of opacity. Magnesium oxide, itself, is, however, commonly not used as the white backing because of its fragility; nor is the white backing placed in actual contact with the sample. Because of these and other sources of error, opacimeters frequently give erroneous results. Standards of opacity made of permanent material serve to check and to calibrate such instruments. Such standards made of opal glass are described, the theory of their application is given, and results of tests by their use reported. It is found that TAPPI opacity corresponds to a reflectance of white backing in contact with the sample of about 0.89.

A New Method for Determining Invertase Activity

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A new method for the determination of yeast invertase has as a basis the determination of the number of enzyme units, termed "invertons," per gram of preparation. The enzyme units are based upon the initial rate of inversion of the sucrose substrate. They are quickly and accurately evaluated, and are of practical significance with respect to the actual performance of the enzyme.

The method has been applied to three different commercial preparations with excellent results.

There are several methods now in use for estimating invertase activity (*4, 7, 9, 11, 12, 13*). These methods have as a basis the determination of either the unimolecular constant k or time values required for a given percentage hydrolysis by a definite amount of invertase preparation. In addition, Nelson and Hitchcock (*7*) have proposed an empirical constant which is proportional to enzyme concentration over a wide range of concentration.

The methods utilizing the unimolecular k are not valid, as has been demonstrated repeatedly by several investigators (*1, 5, 8*). The methods employing time values are sufficiently accurate, but in general are time-consuming with respect to experimental measurements and calculations. The empirical constant of Nelson and Hitchcock (*7*) is not easily evaluated, and while it is proportional to enzyme concentration it is not easily expressed in terms of actual enzyme performance.

In the authors' study of invertase they have developed a method of activity measurement which is characterized by extreme simplicity of measurement and calculation. The method accurately evaluates enzyme activity in terms of the rate at which the invertase hydrolyzes the sucrose, thus giving an activity measure which is directly related to enzyme performance.

It has been established by several workers (*6, 8*) that the initial rate of hydrolysis of sucrose by yeast invertase is directly proportional to the concentration of the invertase. The authors have elaborated on this work by studying the rate of hydrolysis very near the start of the reaction and have shown conclusively that the rate of hydrolysis at zero time—that is, at the very beginning of the inversion—is directly proportional to enzyme concentration over a wide range. Using this as a basis they have defined a rational enzyme unit termed the "inverton." The "inverton" is that amount of yeast invertase which will hydrolyze sucrose at the rate of 5 mg. per minute at zero time, under the specified experimental conditions. Since initial rates are proportional to invertase concentrations, we may use the inverton unit as a measure of the concentration of enzyme in a given preparation. The number of invertons per gram of preparation give a rational and logical measure of the strength of the preparation. This method of treatment has been previously applied to the study of alpha-amylase by Johnston and Jozsa, whose results will soon be published.

Experimental

In order to establish the validity of the inverton, it is necessary to carry out careful measurements of initial rates of inversion.

The measurements were made on a 5 per cent sucrose solution which was buffered to a pH of 4.6 by a Walpole acetate buffer (*2*). The sucrose solution was prepared by dissolving 100 grams of sucrose in distilled water, adding 50 ml. of Walpole acetate buffer of pH 4.6, and making up to 1 liter at 25° C. with distilled water. A commercial enzyme preparation preserved in glycerol was used. This was diluted for use by making up weighed samples to a definite volume with distilled water. The dilute enzyme solutions generally contained from 1 to 10 mg. of original enzyme concentrate per ml. of solution. In carrying out a rate measurement 25 ml. of diluted sample were pipetted at 20° C. into a 200-ml. flask. The sample was placed in a thermostat at 25° C. and after coming to temperature, 25 ml. of a 10 per cent sucrose solution were added at 25° C., noting the time. The sucrose solution was added from a fast pipet and the mixture thoroughly shaken. The mixture was incubated at 25° C. for intervals of 1, 2, 3, 4, 6, 8, and 10 minutes. The reaction was stopped and mutarotation accelerated by the addition of 0.5 ml. of 15 N ammonia. After standing for several minutes (longer than 5 minutes, less than 2 hours) the solutions were polarized in a 4-dm. tube, using a Fric saccharimeter with a Ventzke scale. The initial or blank polarization was determined in each case by polarizing a mixture of 25 ml. of sample, 0.5 ml. of ammonia, and 25 ml. of sucrose solution, mixed in the order named.

The initial reaction mixture corresponds to a 5 per cent sucrose solution, which is the optimum concentration for invertase activity. The data in Table I were used in plotting the rate curves for the preparation used as a standard.

Table I. Rate of Inversion by Standard Invertase

Time	Sucrose Inverted: Invertase Concn. 2.5 mg./cc.		Invertase Concn. 5 mg./cc.		Invertase Concn. 10 mg./cc.
Min.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
1	31	36	67	67	141
2	66	71	139	138	281
3	101	101	206	210	..
4	137	137	278	282	505
6	208	208	417	410	744
8	279	279	540	517	952
10	350	350	665	624	1197

Plotted on a large scale, the rate curves indicate that over the range tested the initial rate of action of the invertase is directly proportional to its concentration. This is illustrated in Figure 1. The results of Table II were obtained from the large-scale curves.

Table II. Initial Inversion Rates of Standard Invertase

Concentration of Invertase Preparation	Rate of Inversion of Sucrose at Zero Time
Mg./ml.	*Mg./min.*
2.5	35
5.0	70
10.0	143

These results enable us to choose a rational enzyme unit which may be applied over the experimental range. In order to obtain a value approximating 100 enzyme units or invertons per gram for the standard commercial sample, the authors chose the inverton as equal to a rate of inversion of sucrose of 5 mg. per minute at zero time at 25° C., under the conditions specified. This gives 112 enzyme units per gram of the standard invertase.

To determine the inverton concentration of a given sample without resorting to rate measurements, it is necessary to

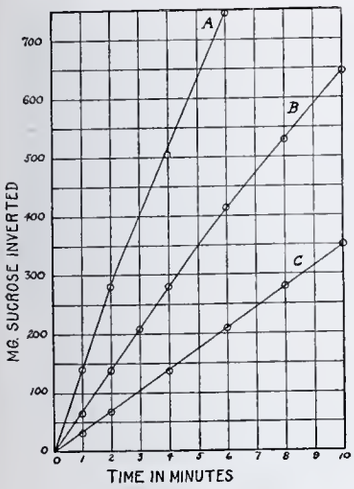

FIGURE 1. RATE CURVES FOR STANDARD INVERTASE

A, 10.0 mg. per ml.
B, 5.0 mg. per ml.
C, 2.5 mg. per ml.

establish a relation between some easily obtainable quantity and the number of invertons present. The amount of sucrose inverted after 0.5 hour at 25° was chosen as the easily obtainable quantity. Dilutions of the standard invertase were made and solutions of known inverton concentration were used as outlined previously, except that the reaction was stopped after 30 minutes in each case instead of after variable time intervals.

Dilutions were made so that the concentration varied from 1.4 to 33.6 invertons per 25 ml. of solution, corresponding to a variation of 0.5 to 12 mg. of standard invertase per 25 ml.

Calibrated glassware (Bureau of Standards) and distilled water were used in all these dilutions in order to insure accuracy. Vosburgh (*10*) found that errors were introduced upon dilution with water containing small amounts of electrolytes. If an accuracy of 1 per cent is to be realized, distilled water must be used. In carrying out the determinations a standard 25-ml. pipet having an outflow time of 35 seconds at 25° C. was used. Time was counted from the moment of introduction of the sucrose. The mixture was shaken vigorously during the addition.

The values of Table III were used in plotting the inverton-sucrose curve shown in Figure 2.

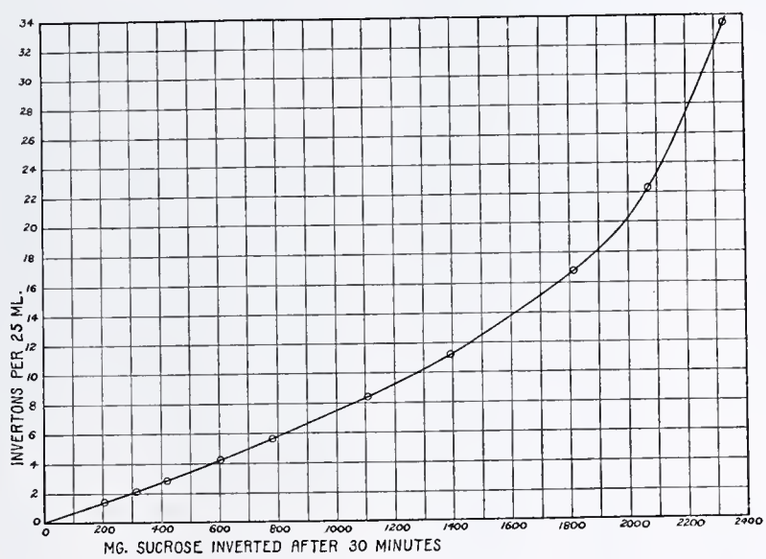

FIGURE 2. INVERTON-SUCROSE CURVE

TABLE III. SUCROSE INVERSION AS FUNCTION OF INVERTON CONCENTRATION

Invertons per 25 Ml.	Sucrose Inverted after 30 Minutes A	B
	Mg.	*Mg.*
1.4	..	209
2.1	315	321
2.8	422	423
4.2	604	606
5.6	782	784
8.4	1107	1115
11.2	1392	1395
16.8	1813	1818
22.4	2072	..
33.6	2331	..

It was found that the curve could be best fitted by two equations. A least-squares solution for the portion of the curve up to 1025 mg. gave the following equation:

$$\log I = 1.0667 \log S - 2.3368$$

I = number of invertons per 25 ml. of sample
S = mg. of sucrose inverted after 0.5 hour reaction at 25° C.

For the range from 1025 to 2000 mg. a logarithmic equation was derived:

$$\log I = 0.0004289\, S + 0.4490$$

S and I have their previous significance.

In using these equations, one first calculates the number of milligrams of sucrose inverted and then chooses the proper equation to fit the sucrose value. The inverton value calculated represents the number of invertons per 25 ml. of diluted sample. It must be calculated to a basis of 1 gram of original sample; so the dilution factor must be applied to the inverton value obtained from the equation. For example, if 10 invertons are calculated per 25 ml. of diluted sample and the diluted sample contains 125 mg. of original preparation per 25 ml., there are 80 invertons per gram of original sample.

TABLE IV. RATE OF INVERSION BY INVERTASE NO. 1

(2.5 mg. of invertase preparation per ml. used in experiments A, B, and C; 5 mg. per ml. in D and E)

	Sucrose Inverted						
	A	B	C	Av.	D	E	Av.
Min.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
1	41.1	41.1	36.0	39.4	72.0	82.1	77.1
2	71.8	71.8	72.0	71.9	144	144	144
3	108	113	108	110	211	221	216
4	139	144	144	142	278	277	278
6	200	216	206	207	412	411	412
8	277	282	273	277	535	539	537
10	344	349	343	345	659	657	658

In order to establish the method of measurement it was necessary to study the rate curves of other commercial invertases and investigate the constancy of the calculated inverton value on dilution of the enzyme preparation. Three commercial invertases were studied. It was found that the activity of all three invertases could be accurately determined by applying the inverton method. The results obtained with commercial invertase No. 1 are given in Table IV.

The data for invertase No. 1 were plotted in Figure 3. The initial slopes of these rate curves showed the same property as those of the standard curves. The invertase concentration was directly proportional to the rate of inversion at zero time. In order to check the behavior of the preparation on dilution the data given in Table V (invertase No. 1) were obtained.

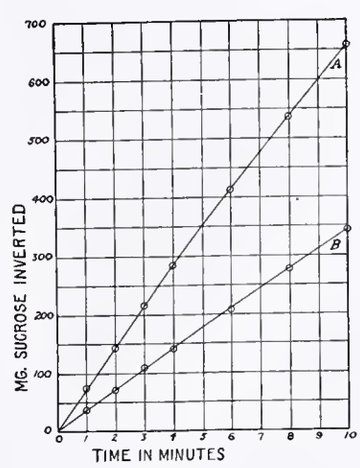

FIGURE 3. RATE CURVES FOR INVERTASE NO. 1

A, 5.0 mg. per ml.
B, 2.5 mg. per ml.

When plotted, the results in Table V gave the straight line of Figure 4, showing clearly the linear relation between concentration and number of invertons.

Another commercial invertase, No. 2, was purchased in the open market and checked exactly as invertase No. 1 (Table VI

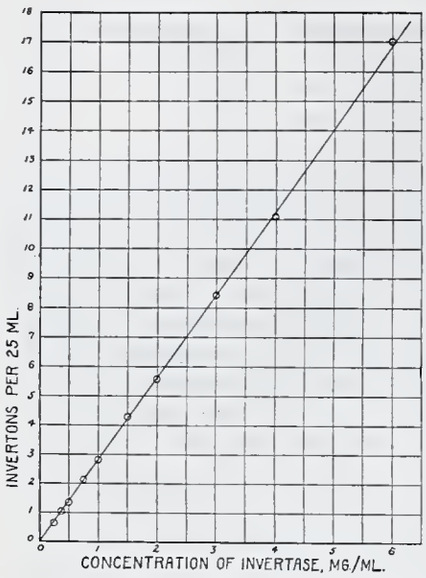

FIGURE 4. DILUTION CURVE FOR INVERTASE NO. 1

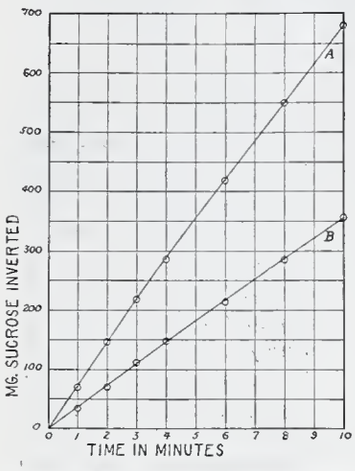

FIGURE 5. RATE CURVES FOR INVERTASE NO. 2

A, 5.0 mg. per ml.
B, 2.5 mg. per ml.

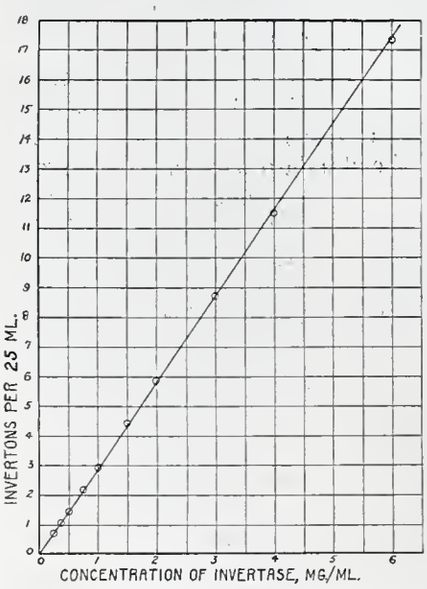

FIGURE 6. DILUTION CURVE FOR INVERTASE NO. 2

and Figure 5). The same concordance with the standard invertase was observed.

The dilution check was carried out as before; the data are given in Table V (invertase No. 2) and the plot in Figure 6. The same proportionality between concentration of enzyme and number of invertons is observed.

A third commercial preparation was checked as in the other cases. The results agreed very well with the data on the other invertases. The data for the rate curves are given in Table VII and the rate-curve plot in Figure 7. The dilution data are found in Table V (invertase No. 3) and the plot in Figure 8.

As a further check of the uniformity of behavior, the three invertases were checked over the 30-minute period by establishing the form of the 30-minute curve for each preparation. The three curves were essentially superposable over the entire period.

The results are tabulated in Table VIII and are plotted in Figure 9. In each case a concentration of preparation was chosen which would correspond to the same number of invertons.

The various experiments show clearly that the number of invertons in a given weight of preparation is directly proportional to the concentration of the invertase in the preparation. The data also indicate that the method of measurement is accurate and of general applicability to the determination of yeast invertase.

Nelson and Hitchcock (*7*) found that certain invertase preparations behaved in an abnormal manner. The abnormality was evidenced by a dropping off of the rate of inversion after approximately 20 per cent of the sucrose had been hydrolyzed in a 10 per cent sucrose solution. They were unable to ascribe this to any method of preparation of the enzyme concentrate. Fassnacht (*3*) has elaborated on this work and has given a method for the preparation of abnormal yeast invertase. The authors attempted to prepare an abnormal invertase but have not been able to duplicate Fassnacht's results. They are continuing the work with a view to clearing up the discrepancies.

TABLE V. RELATION BETWEEN INVERTASE AND INVERTON CONCENTRATIONS

Concentration of Invertase	Invertons per 25 Ml. Experimentally Determined		
	Invertase No. 1	Invertase No. 2	Invertase No. 3
Mg./ml.			
6.0	17.04	17.35	17.27
4.0	11.10	11.52	11.39
3.0	8.44	8.72	8.68
2.0	5.59	5.89	5.83
1.5	4.30	4.47	4.38
1.0	2 83	2.97	2.91
0.75	2.14	2.21	2.18
0.50	1.37	1.48	1.43
0.38	1.03	1 09	1.06
0.25	0.67	0.74	0.71

TABLE VI. RATE OF INVERSION BY INVERTASE NO. 2

(2.5 mg. of invertase preparation per ml. used in experiments A and B; 5 mg. per ml. in C).

	Sucrose Inverted			
	A	B	Av.	C
Min.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
1	35.8	35.8	35.8	71.7
2	76.8	61.4	69.1	148
3	113	107	110	220
4	148	135	142	287
6	210	215	213	420
8	287	282	285	552
10	363	348	356	681

TABLE VII. RATE OF INVERSION BY INVERTASE NO. 3

(25 mg. of invertase preparation per ml. used in experiments A and B; 5 mg. per ml. in C and D)

	Sucrose Inverted					
	A	B	Av.	C	D	Av.
Min.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
1	35.9	35.9	35.9	77	77	77
2	77.0	77.0	77.0	149	149	149
3	113	113	113	226	216	221
4	149	149	149	287	287	287
6	226	215	221	416	416	416
8	287	287	287	549	549	549
10	359	359	359	677	672	675

TABLE VIII. UNIFORMITY OF INVERSION OF SUCROSE BY COMMERCIAL INVERTASE PREPARATIONS

	Invertase No. 1[a]			Invertase No. 2[b]			Invertase No. 3[c]		
	A	B	Av.	A	B	Av.	A	B	Av.
Min.									
2	143	143	143	143	149	146	139	139	139
4	276	287	282	282	282	282	267	272	270
6	404	415	410	415	421	418	400	400	400
8	537	543	540	550	544	547	529	534	532
10	655	660	658	671	672	672	652	652	652
14	880	896	888	906	906	906	883	875	879
17	1044	1055	1050	1065	1073	1069	1037	1042	1040
20	1190	1208	1199	1213	1221	1217	1191	1196	1194
25	1423	1433	1428	1449	1452	1451	1422	1422	1422
30	1607	1637	1622	1648	1642	1645	1622	1622	1622

[a] Concentration, 5 mg. per ml.
[b] Concentration, 4.914 mg. per ml.
[c] Concentration, 4.831 mg. per ml.

The preparation of abnormal invertase was attempted in order to test the method as completely as possible. It is apparent from the nature of the invertase method that in order to measure an abnormal invertase accurately it is only necessary to determine a dilution curve for the preparation in question. If the curve deviates from a straight line it is evident that one is dealing with an abnormal preparation. To measure the inverton content, a dilution should be chosen

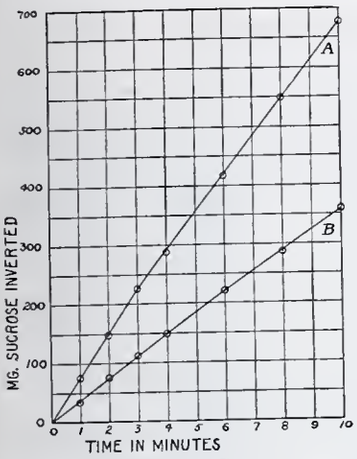

FIGURE 7. RATE CURVES FOR INVERTASE NO. 3

A, 5.0 mg. per ml.
B, 2.5 mg. per ml.

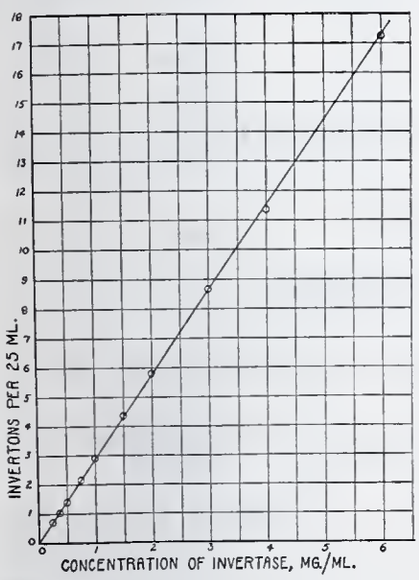

FIGURE 8. DILUTION CURVE FOR INVERTASE NO. 3

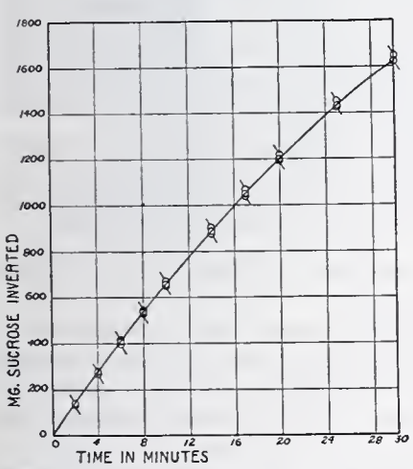

FIGURE 9. COMPARISON OF RATE CURVES FOR SOLUTIONS OF DIFFERENT INVERTASES CONTAINING THE SAME NUMBER OF INVERTONS

○, Invertase No. 1
◡, Invertase No. 2
◠, Invertase No. 3

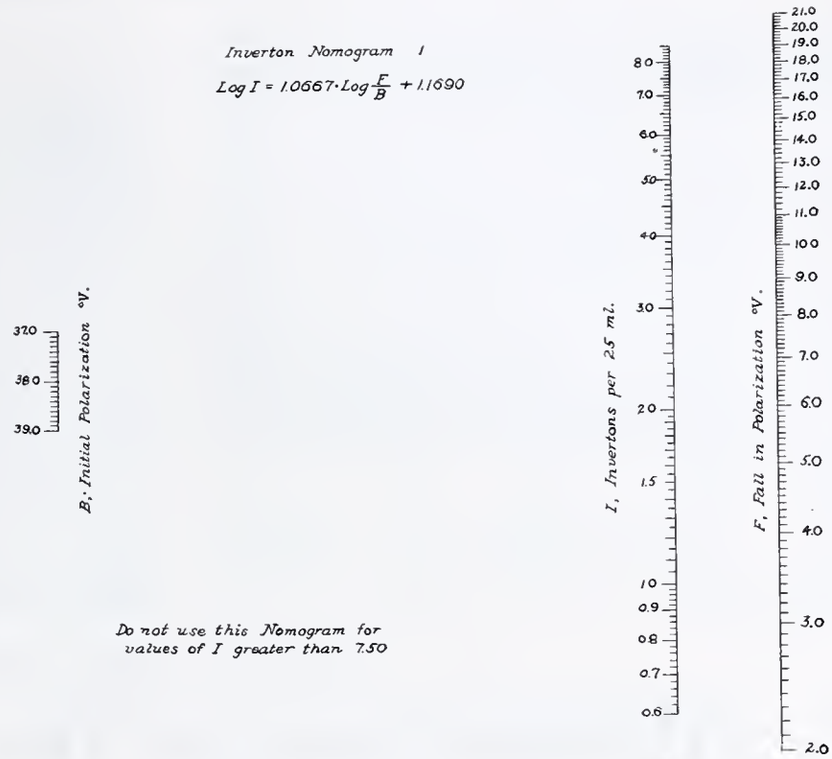

FIGURE 10. INVERTON NOMOGRAM

For *I* values less than 7.50

which corresponds to the linear portion of the curve. Any preparation not known to be normal should be checked in this manner. It seems likely that few abnormal preparations will be found in commercial samples.

CALCULATIONS

The number of milligrams of sucrose inverted was calculated by the following formula:

$$S = 2500 \times \frac{F}{V} \qquad (1)$$

where

F = fall in polarization after inversion
V = drop in polarization upon complete inversion

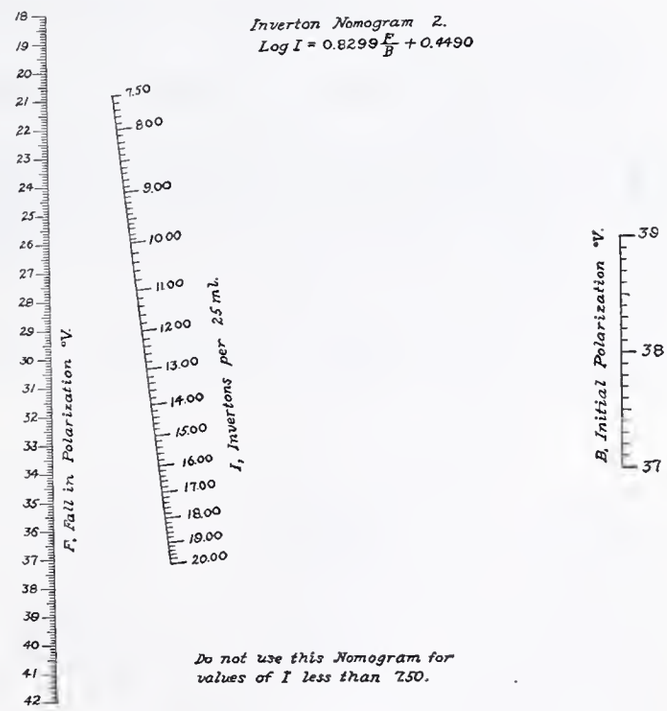

FIGURE 11. INVERTON NOMOGRAM

For *I* values greater than 7.50

V was calculated by the Hudson formula:

$$V = \frac{B}{100}\left(141.7 - \frac{t}{2}\right) \qquad (2)$$

where B = initial or blank rotation
t = temperature in ° C.

The Hudson formula has recently been revised, but the difference is negligible in comparison with the authors' experimental error of 2 per cent.

The two formulas previously given for calculating the number of invertons are easily modified into a form more suitable for rapid calculation. Since the temperature is maintained constant at 25° C., the Hudson formula reduces to

$$V = 1.292\,B \qquad (3)$$

If Formula 3 is substituted into 1 and the resulting equation into the original inverton formulas, and the resulting equations are simplified, Formulas 4 and 5 are obtained:

$$\log I = 1.0667 \log \frac{F}{B} + 1.1690 \quad (4)$$

for values of I up to 7.50

$$\log I = 0.8299 \frac{F}{B} - 0.4490 \quad (5)$$

for values of I greater than 7.50

Formulas 4 and 5 are easily represented by nomograms, which were constructed by the usual method (Figures 10 and 11). The inverton values are read by aligning the point representing initial polarization with that representing fall in polarization and noting the point at which the line crosses the inverton scale.

Acknowledgment

The authors wish to thank Charles N. Frey for his aid and interest in this work.

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Determination of Mercaptans in Hydrocarbon Solvents

An Improvement of the Silver Nitrate Method

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A PROCEDURE has been described by Borgstrom and Reid (*1*) for determining mercaptans, involving the formation of silver mercaptide by excess silver nitrate which is titrated back with ammonium thiocyanate, using ferric alum as an indicator. This analog of a known method of chloride determination revealed some difficulties in use, as reported by Malisoff and Marks (*3*) and in private communications (*2*). An example of the oscillation in results when the method is applied literally is given in Table I.

Table I. Analysis of *n*-Amyl Mercaptan in Naphtha for Mercaptan Sulfur

Concentration (calcd.)	Mercaptan Sulfur Found: Borgstrom-Reid method[a]	Mercaptan Sulfur Found: Modified method[b]
%	%	%
0.162	0.196–0.199	0.158–0.166
0.316	0.315–0.399	0.314–0.324
0.738	0.664–0.762	0.730–0.750

[a] Range of from 4 to 6 analyses (each analysis = 2 titrations).
[b] Two or more analyses.

At the higher mercaptan concentrations the averages seem to line up better, but one must have more than two analyses per sample and even then may be in doubt. An effort has been made to set up a series of safeguards and a sharper definition of conditions to insure a better degree of reproducibility.

Experimental

Materials. The mercaptans and solvents have been described by Malisoff and Marks (*3*). Besides these, phenyl and *p*-tolyl mercaptans were obtained from the Eastman Kodak Company and had boiling points of 70° to 71° C. at 15 mm. and melting points of 41° to 43° C., respectively. The inorganic reagents were Baker's c. p. analyzed.

Procedure. The tests are performed in glass-stoppered Erlenmeyer flasks. To known (weighed) amounts of mercaptan solutions kept in the dark for as short a period as possible, add 5 to 10 cc. of methanol and an excess of standard 0.005 N silver nitrate. Shake well and add 2 cc. of standard ferric alum indicator. Titrate with 0.005 N ammonium thiocyanate to a very faint pink. Then add a small excess of silver nitrate solution and titrate back again with thiocyanate until the pink appears. The final result is taken as the end point. Constant shaking is necessary throughout, and care must be taken not to confuse the faint color of the end point with the slight tint due to the presence of ferric alum. If in doubt, repeat the treatment with excess of silver nitrate and titration with thiocyanate.

Stock ferric alum solution is made up of 40 grams of ferric alum and 20 cc. of 6 N nitric acid per 100 cc. It is boiled to remove any free nitrogen oxides and then diluted with 3 parts of water to 1 of stock to make up the actual standard indicator.

Using the procedure as outlined, analytical data have been obtained as shown in Table II.

Purity of Mercaptans. The purity and the stability of the mercaptans were tested in hydrocarbon solution under varying conditions. Amyl mercaptan was the purest and most reliable of those studied. The principal impurities are disulfides which themselves do not affect the analytical method. Mercaptans, especially the aromatic ones, change readily to disulfides by oxidation. The effect is marked in sunlight, and is sufficient to account for discrepancies in analyses carried on before and after exposure to ordinary daylight. The effect also appears to be greater in naphtha solutions than in benzene.

Table III indicates the effect of exposure to direct ordinary daylight in a southeast window. It is apparent that within a month it is possible to miss all of certain mercaptans in a hydrocarbon solution containing originally about 0.3 per cent of mercaptan sulfur.

[1] Present address, Department of Physiological Chemistry, University of Pennsylvania, Philadelphia, Pa.

Table II. Determination of Mercaptan Sulfur by Modified Method

Mercaptan	Solvent	Mercaptan Sulfur: Present (calcd.)	Found	Deviation of check determinations
		%	%	%
n-Amyl	Naphtha	0.748	0.733	±1.6
	Naphtha	0.322	0.319	±1.8
	Naphtha	0.162	0.164	±2.4
	Naphtha	0.063	0.063	±0.8
	Amylene	0.301	0.302	±0.5
	Heptane + Octane	0.324	0.319	±0.4
	Benzene	0.285	0.280	±2.0
	Benzene	0.164	0.161	±1.0
Isoamyl	Naphtha	0.337	0.328	±0.8
	Naphtha	0.070	0.067	±0.9
n-Butyl	Naphtha	0.325	0.301[a]	±1.3
Isobutyl	Naphtha	0.309	0.306	±1.6
	Naphtha	0.060	0.060	±0.2
n-Propyl	Naphtha	0.311	0.308	±1.6
	Naphtha	0.060	0.059	±1.4
n-Heptyl	Naphtha	0.320	0.318	±1.0
	Naphtha	0.063	0.064	±1.5
Benzyl	Naphtha	0.347	0.350	±2.2
	Naphtha	0.063	0.064	±1.7
	Benzene	0.302	0.310	±1.0
Phenyl	Naphtha	0.356	0.312[b]	±5.0
	Benzene	0.318	0.290	±0.1
p-Tolyl	Naphtha	0.329	0.275[c]	±5.3
	Benzene	0.321	0.283	±3.0

[a] 0.013 per cent of sulfur found to be R_2S_2.
[b] 0.011 per cent sulfur found to be R_2S_2.
[c] 0.020 per cent sulfur found to be R_2S_2.

Table III. Effect of Light Exposure on Mercaptans

[Solutions exposed in sealed 120-cc. (4-oz.) cylindrical glass bottles]

RSH	Solvent	Exposure[a]	Mercaptan Sulfur: Original	Final	Changed
		Days	%	%	%
n-Amyl	Benzene	27	0.282	0.273	0.009
	Heptane Octane	27	0.312	0.297	0.015
	Naphtha	17	0.330	0.274	0.056
	Naphtha	5	0.066	0.005	0.061
	80% Naphtha 20% Amylene	17	0.061	0.002	0.059
Isoamyl	Naphtha	17	0.335	0.304	0.031
	Naphtha	14	0.067	0.005	0.062
n-Butyl	Naphtha	27	0.298	0.181	0.117
	Naphtha	14	0.060	0.007	0.053
Isobutyl	Naphtha	17	0.300	0.268	0.032
	Naphtha	14	0.060	0.003	0.057
n-Propyl	Naphtha	27	0.310	0.162	0.148
	Naphtha	14	0.059	0.003	0.056
n-Heptyl	Naphtha	14	0.064	0.004	0.060
Benzyl	Benzene	26	0.310	0.307	0.003
	Heptane Octane	26	0.319	0.228	0.091
	Naphtha	37	0.064	0.000	0.064
Phenyl	Benzene	27	0.287	0.169	0.118
	Benzene	17	0.298	0.220	0.078
	Naphtha	24	0.304	0.000	0.304
p-Tolyl	Benzene	27	0.282	0.225	0.057
	Naphtha	27	0.275	0.000	0.275

[a] Exposed at relatively the same time.

Table IV indicates that prolonged storage in a laboratory cabinet with glass doors and no direct sunlight results in serious changes and explains the provision for dark storage for the shortest possible time.

Concentration of Mercaptans. When the concentration of mercaptan sulfur is 0.150 per cent or greater the weighed sample is diluted to a definite volume and an aliquot portion used for analysis. A 5- or 10-cc. portion of a mercaptan sulfur concentration of about 0.075 per cent is convenient, since in this range the quantity of silver mercaptide precipitated is moderate and the volume of solution in the 250-cc. Erlenmeyer flask is a convenient one.

Diluents. Methanol is preferred as a diluent, since it is soluble in both water and oil and therefore improves mutual interpenetration and because it is readily available in a pure state.

Emulsion Breaking. The precipitation of silver mercaptides favors emulsion formation. This is counteracted by working with the low dilutions recommended and by the addition of methanol prior to that of silver nitrate. In some cases it may be wise to increase the amount of methanol.

Masking of End Point. Colored mercaptides or the oil itself may occasionally introduce difficulty in reading the end point. In such cases an actual physical separation of the oil is made and the mercaptide precipitate is filtered off and washed. The original solution and the wash liquor are titrated.

Table IV. Effect of Storage of Naphtha Solutions of Mercaptans in Laboratory Cabinet

Kind	Time	Mercaptan Sulfur: Original	Final	Changed
	Months	%	%	%
Phenyl	2	0.368	0.295[a]	0.073
	10	0.368	0.185	0.183
n-Butyl	14	0.311	0.241	0.070
n-Amyl	1	0.366	0.329[b]	0.037
	9	0.366	0.181	0.185
	6	0.275	0.261[c]	0.014

[a] 0.055 per cent sulfur as R_2S_2.
[b] 0.029 per cent sulfur as R_2S_2.
[c] Dark storage.

Light for Titration. Precision is gained by working in bright daylight. Reproduction may be poor on gray days unless a daylight lamp is used. The standardization of the ferric alum indicator is advantageous.

Discussion

The principal changes in the Borgstrom and Reid procedure are: inclusion of precautions concerning the storage of mercaptan samples, adoption of a uniform dilution method, employment of more dilute standard solutions, standardization of the ferric alum indicator, provisions for minimizing emulsions, provision for minimizing masking of color, and reduction of the time of operation (direct titration, without shaking period). The erratic results when the above factors are not considered are thus eliminated.

Table V

Mercaptan	Mercaptan Sulfur: Calculated	Found	R_2S_2	Total Sulfur Found
	%	%	%	%
p-Tolyl	0.189[a]	0.118[b]	0.077	0.195
Phenyl	0.210[a]	0.125[b]	0.094	0.219

[a] Average of 3 analyses.
[b] Average of 2 analyses.

Working with this procedure, using known solutions of aliphatic mercaptans, it is possible to account for 97.3 to 102.7 per cent of the mercaptan present with a maximum deviation of less than 2.4 per cent. In the case of the aromatic mercaptans only 83.6 to 91.2 per cent was determined because part of the mercaptans had changed to disulfides. An effort made to check this by slow reduction with zinc and acetic acid, followed by titration of the resulting mercaptan, led to a satisfactory sulfur balance as shown in Table V.

Table VI. Duplicate Analyses of Commercial Naphthas

Kind	Mercaptan Sulfur	
	%	%
Straight run	0.004	0.004
	0.008	0.008
Cracked distillate	0.008	0.007
	0.001	0.001
	0.008	0.008
	0.017	0.016
	0.036	0.039
	0.052	0.054
Vapor phase cracked	0.017	0.018
	0.031	0.035

The results are a little high, probably on account of the method for determining disulfides. This was proved by

extracting the mercaptans with caustic-methanol and redetermining them in the extract. The results were for *p*-tolyl mercaptan, 0.118 per cent on both samples, and for phenyl mercaptan, 0.125 per cent directly and 0.123 per cent in the extract.

Experiences with commercial naphthas are appended (Table VI). These show the breakdown of sensitivity at 0.001 per cent of mercaptan sulfur at very low concentrations and a variation of 0.004 per cent at a concentration of 0.035 per cent.

Literature Cited

(1) Borgstrom and Reid, Ind. Eng. Chem., Anal. Ed., 1, 186–7 (1929).
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Determination of Gas, Coke, and By-Products of Coal

Evaluation of Laboratory Assay Tests

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Two small-scale, laboratory, high-temperature assay tests and one low-temperature assay test for determination of yields of gas, coke, and by-products of coal have been applied to 20 to 30 coals. Check limits have been established for duplicate determinations on the same coal by the same laboratory.

Yields of gas, coke, and by-products by the laboratory tests have been correlated with yields obtained by the BM-AGA carbonization test. The factors for converting the yields obtained by the small-scale laboratory tests into those obtained by the BM-AGA carbonization test vary appreciably with different coals.

In connection with a survey of gas-, coke-, and by-product–making properties of American coals being made at the Pittsburgh Experiment Station of the United States Bureau of Mines (*2*, *3*), the following small-scale laboratory assay tests have been applied to 20 to 30 coals (Table I): United States Steel Corporation dry-distillation test (*8*), Fuel Research Board (British) high-temperature assay (*6*), and Fischer low-temperature assay (*5*). The bureau studied the duplicability of the tests and their correlation with the Bureau of Mines–American Gas Association (BM-AGA) test (*3*), in which charges of 36 to 45 kg. (80 to 100 pounds) of coal are carbonized in a cylindrical retort 32.5 cm. (13 inches) in diameter.

A correlation of the yields of gas, coke, and by-products as obtained by these various methods should permit evaluation of these small-scale laboratory tests for predicting the probable yields from a given coal in commercial carbonization practice. An advantage of this correlation is that the BM-AGA carbonization tests were conducted under closely controlled and comparable conditions and not under varying conditions, as would occur in different commercial gas and coking plants.

United States Steel Corporation Test

The procedure used was that published by the Chemists' Committee of the United States Steel Corporation (*8*), in which 20 grams of dry coal passing a No. 35 sieve are heated progressively up to 900° C. in a gas-fired combustion furnace. A transparent quartz tube was substituted for the glass tube specified, because glass tubes often failed at the carbonization temperature.

After charging, a well-fitting Pyrex-glass tube, 95 mm. in length, is inserted into the open end of the quartz tube. The inner glass tube collects that portion of the tar and combined ammonia that does not pass into the recovery train. When the test is completed, the quartz tube with its contents is weighed. The inner glass tube is removed, boiled in water to dissolve combined ammonia, immersed and scrubbed in acetone to remove tar, and ignited. The open end of the quartz tube is ignited to burn off any tar that may have collected. The glass tube is replaced and the quartz tube with its contents is weighed. The decrease in weight represents the tar and combined ammonia present in the distillation tube and is added to that recovered in the tar filter.

When the published method was used tar yields were low, because of excessive cracking of the tar in the end of the quartz tube. At the suggestion of the Central Laboratory of the Illinois Steel Company, Joliet, Ill., the temperature of the tar end of the quartz tube, which projects out of the furnace, was lowered by means of an asbestos shield provided with a hole to fit snugly around the distillation tube at the outer end of the furnace. With this modification, tar yields were obtained which were more comparable to those obtained in coke-oven practice.

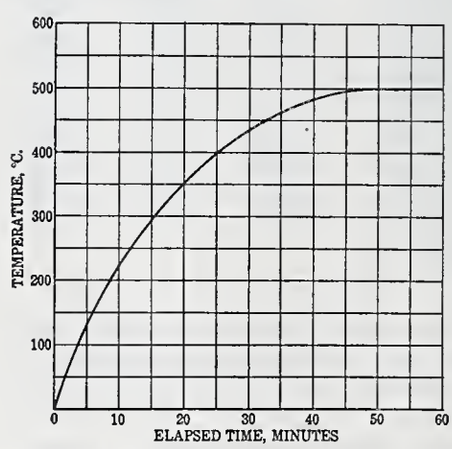

Figure 1. Time-Temperature Curve for Fisher Low-Temperature Test

The freezing method for determination of light oil was used in this investigation.

Fuel Research Board Test

In the Fuel Research Board test the coal is heated in an electric furnace to 900° C. A 10-gram sample of air-dry coal, passing a No. 60 sieve, was used instead of the 20-gram sample specified in the published method, as trouble was ex-

Table I. Source and Analyses of Coals, As-Received Basis

Coal No.	State	County	Mine	Bed	Laboratory No.	Proximate Analysis: Moisture	Volatile matter	Fixed carbon	Ash	Ultimate Analysis: S	H	C	N	O	Calorific Value
						%	%	%	%	%	%	%	%	%	B. t. u./lb.
1W	Pa.	Allegheny	Warden	Pittsburgh (washed)	A54234	2.4	34.5	57.2	5.9	1.0	5.7	78.3	1.6	7.5	13,910
2	Ky.	Letcher	Consolidation No. 204	Elkhorn	A55799	2.2	36.6	59.0	2.2	0.6	6.1	80.9	1.5	8.7	14,410
3	Va.	Wise	Roda No. 3	Taggart	A59032	1.7	36.1	59.5	2.7	0.6	5.9	82.5	1.5	6.8	14,770
4	Md.	Garrett	Arnold	Davis or Upper Freeport	A61732	1.4	22.1	66.7	9.8	1.5	5.0	77.7	1.5	4.5	13,820
					A62799	1.5	27.7	63.3	7.5	1.2					14,070
5	60% No. 4; 40% No. 1W				A63222	1.3	33.3	60.0	5.4	0.9	5.4	80.0	1.6	6.7	14,220
6	20% No. 4; 80% No. 1W														
7	Ala.	Jefferson	Flat Top	Mary Lee (unwashed)	A70035	1.2	27.9	55.0	15.9	0.8	4.6	71.4	1.5	5.8	12,600
8	Ala.	Jefferson	Flat Top	Mary Lee (washed)	A66398	4.2	27.6	59.9	8.3	0.8	5.1	76.2	1.6	8.0	13,550
9	Pa.	Fayette	Edenborn	Pittsburgh	A67653	1.9	33.6	57.0	7.5	1.0	5.2	77.4	1.6	7.3	13,910
10	Ill.	Franklin	New Orient No. 1	No. 6	A69265	7.9	32.1	47.7	12.3	0.8	5.1	65.5	1.4	14.9	11,540
11	B. C.		Michel	B	A69650	1.4	27.0	65.4	6.2	0.6	4.9	80.8	1.3	6.2	14,240
12	Pa.	Fayette	Allison	Pittsburgh	A71770	1.0	33.6	56.9	8.5	1.3	5.3	77.0	1.6	6.3	13,820
13	Ala.	Walker	Empire	Black Creek	A72180	3.1	36.0	58.3	2.6	1.1	5.7	79.2	1.7	9.7	14,190
14	W. Va.	Logan	Boone No. 2	Chilton	A73643	2.2	36.2	57.3	4.3	0.6	5.4	79.3	1.5	8.9	14,200
15	W. Va.	Kanawha	Point Lick No. 4	No. 2 Gas	A74912	1.9	38.8	56.6	2.7	0.9	5.5	80.3	1.4	9.2	14,450
16	W. Va.	Boone	Spruce River No. 4	Alma	A76674	2.1	37.7	53.1	7.1	1.8	5.4	76.8	1.5	7.4	13,810
17	Ala.	Jefferson	Wylam No. 8	Pratt (unwashed)	A78090	1.5	30.1	59.2	9.2	0.7	5.0	77.1	1.6	6.4	13,730
18	Ala.	Jefferson	Wylam No. 8	Pratt (washed)	A79220	3.0	31.5	62.4	3.1	0.6	5.5	81.5	1.7	7.6	14,510
19	Utah	Carbon	Columbia	Lower Sunnyside	A80086	4.6	38.8	50.6	6.0	1.0	5.7	72.9	1.5	12.9	13,030
20	Pa.	Allegheny	Wildwood	Thick Freeport	A81851	2.2	36.3	55.2	6.3	1.3	5.5	76.9	1.5	8.5	13,870
21	Ky.	Muhlenberg	Green River	Green River	A83760	10.1	36.2	47.0	6.7	2.5	5.8	66.8	1.5	16.7	11,980
22	W. Va.	Marion	Consolidation No. 63	Pittsburgh	A85140	1.9	37.3	54.8	6.0	0.6	5.5	77.9	1.6	8.4	14,010
23	W. Va.	McDowell	Consolidation No. 251	Pocahontas No. 4	A87426	0.8	15.4	79.0	4.8	0.5	4.3	86.7	1.1	2.6	14,870
24	20% No. 23; 80% No. 22				A88814	1.3	32.5	60.3	5.9	0.6	5.2	80.0	1.5	6.8	14,170
25	40% No. 23; 60% No. 22				A90238	1.4	28.3	64.8	5.5	0.6	5.0	81.2	1.5	6.2	14,330
26	W. Va.	Raleigh	Cranberry No. 3	Sewell	A90539	1.3	20.8	75.8	2.1	0.8	4.9	86.8	1.7	3.7	15,190
27	W. Va.	Fayette	Summerlee	Sewell	A91200	1.9	26.5	69.2	2.4	0.5	5.2	84.6	1.6	5.7	14,970
28	Pa.	Allegheny	Warden	Pittsburgh	A94612	1.8	35.1	57.7	5.4	0.9	5.3	79.0	1.6	7.8	14,140
28A	Pa.	Allegheny	Warden	Pittsburgh	A93057	2.6	35.2	56.6	5.6	0.9	5.4	78.4	1.7	8.0	14,000
29	20% No. 26; 80% No. 28A				A94613	1.8	32.0	61.4	4.8	1.0	5.3	80.1	1.6	7.2	14,320
30	20% No. 27; 80% No. 28				A95370	1.9	33.6	59.8	4.7	0.9	5.3	80.1	1.7	7.3	14,330

Table II. Duplicate Determinations for 20 Coals Carbonized by United States Steel Corporation Test

(As-received basis)

Coal No.	Coke %	Coke Diff.	Tar %	Tar Diff.	Water (Liquor) %	Water (Liquor) Diff.	Light Oil %	Light Oil Diff.	Gas by Difference[a] %	Gas by Difference[a] Diff.	Free NH_3 %	Free NH_3 Diff.	Combined NH_3 %	Combined NH_3 Diff.	Gas, as Measured (Air Free)[b] Cu. ft./t. coal	Gas, as Measured Diff.	Gross Heating Value of Gas B. t. u./lb. coal	Gross Heating Value of Gas Diff.
11	75.71	0.11	3.22	0.02	5.10	0.13	1.07	0.07	14.50	0.04	0.243	0.013	0.007	0.006	10,760	10	2940	...
	75.60		3.24		5.23		1.00		14.54		0.230		0.013		10,750		c	
12	73.45	0.16	4.63	0.02	5.78	0.02	1.30	0.01	14.08	0.12	0.310	0.005	0.030	0.013	10,530	110	2940	80
	73.61		4.61		5.76		1.29		13.96		0.305		0.043		10,640		3020	
13	68.73	0.13	4.65	0.03	8.95	0.37	1.48	0.14	15.43	0.13	0.322	0.005	0.040	0.005	10,980	150	3290	170
	68.86		4.62		8.58		1.62		15.56		0.317		0.045		10,830		3120	
14	69.97	0.10	5.39	0.25	7.32	0.01	1.35	0.01	15.43	0.12	0.255	0.004	0.057	0.005	10,870	30	3210	10
	70.07		5.14		7.31		1.36		15.55		0.259		0.062		10,840		3200	
15	68.85	0.00	5.30	0.11	7.07	0.34	1.68	0.07	16.48	0.34	0.257	0.003	0.048	0.027	11,430	10	3370	20
	68.85		5.19		7.41		1.75		16.14		0.260		0.075		11,420		3390	
16	69.38	0.04	5.36	0.15	7.91	0.08	1.40	0.10	15.08	0.01	0.230	0.002	0.046	0.010	10,590	60	3130	...
	69.34		5.21		7.99		1.50		15.09		0.228		0.056		10,530		c	
17	74.94	0.26	4.23	0.04	5.76	0.00	1.03	0.03	13.40	0.22	0.314	0.000	0.010	0.002	10,150	30	2900	10
	74.68		4.27		5.76		1.00		13.62		0.314		0.008		10,180		2910	
18	72.54	0.07	4.45	0.03	7.12	0.05	1.23	0.03	14.07	0.02	0.329	0.000	0.011	0.004	11,030	70	3190	10
	72.61		4.42		7.07		1.20		14.09		0.329		0.007		11,100		3200	
19	63.88	0.16	4.82	0.23	11.33	0.13	1.32	0.04	17.76	0.24	0.355	0.012	0.014	0.002	10,730	60	3150	10
	63.72		5.05		11.46		1.36		17.52		0.367		0.012		10,670		3140	
20	70.33	0.27	5.20	0.13	7.53	0.17	1.43	0.17	14.53	0.13	0.239	0.003	0.070	0.016	10,250	0	3040	40
	70.06		5.33		7.70		1.26		14.66		0.242		0.054		10,250		3000	
21	60.89	0.18	4.27	0.14	18.29	0.08	1.09	0.08	14.09	0.12	0.407	0.006	0.009	0.003	9,290	30	2510	0
	61.07		4.13		18.21		1.01		14.21		0.413		0.006		9,260		2510	
22	69.44	0.01	5.93	0.04	7.37	0.16	1.34	0.01	15.35	0.16	0.310	0.005	0.042	0.005	10,680	0	3240	0
	69.43		5.97		7.21		1.33		15.51		0.305		0.037		10,680		3240	
23	86.27	0.14	1.28	0.14	2.40	0.04	0.53	0.01	9.23	0.07	0.173	0.000	0.016	0.005	10,060	130	2430	20
	86.13		1.42		2.36		0.52		9.30		0.173		0.011		10,190		2450	
24	73.01	0.22	4.82	0.03	6.19	0.17	1.07	0.07	14.44	0.09	0.309	0.002	0.006	0.003	10,490	160	2940	60
	73.23		4.79		6.02		1.14		14.35		0.311		0.009		10,650		3000	
25	75.81	0.05	3.90	0.08	5.68	0.07	1.12	0.13	13.02	0.09	0.286	0.000	0.034	0.007	10,080	50	2810	30
	75.86		3.82		5.75		0.99		13.11		0.286		0.041		10,030		2780	
26	81.99	0.01	2.36	0.07	3.59	0.10	0.71	0.06	10.82	0.08	0.272	0.001	0.040	0.002	10,970	140	2880	20
	81.98		2.29		3.69		0.77		10.74		0.273		0.038		10,830		2860	
27	77.20	0.13	3.72	0.15	4.94	0.00	0.76	0.04	12.94	0.32	0.219	0.005	0.076	0.003	10,560	100	3020	30
	77.33		3.87		4.94		0.80		12.62		0.224		0.073		10,660		3050	
28	71.31	0.27	5.23	0.04	6.79	0.01	1.11	0.06	14.89	0.14	0.312	0.009	0.032	0.003	10,570	180	3050	20
	71.58		5.19		6.80		1.05		14.75		0.303		0.035		10,750		3070	
29	72.39	0.24	5.32	0.11	7.10	0.09	1.15	0.13	13.40	0.16	0.309	0.004	0.023	0.000	10,240	50	2930	20
	72.63		5.21		7.01		1.28		13.24		0.313		0.023		10,290		2950	
30	72.12	0.06	5.18	0.14	6.67	0.02	0.97	0.10	14.44	0.21	0.302	0.001	0.036	0.004	10,570	60	3040	30
	72.06		5.32		6.69		1.07		14.23		0.301		0.032		10,630		3070	
Av. difference		0.13		0.10		0.10		0.07		0.14		0.004		0.006		70		30
Max. difference		0.27		0.25		0.37		0.17		0.34		0.013		0.027		180		170

[a] H_2S-free; CO_2 included; scrubbed free of light oil.
[b] H_2S-free; CO_2 included; scrubbed free of light oil; saturated with water vapor at 60° F. and 30 inches Hg.
[c] Not determined.

perienced from excessive swelling of some coals during carbonization when the larger charge was used.

It is difficult to determine accurately the water in the tar-water mixture collected in the U-tube of the recovery train following the published method. Distillation (7) with toluene as a solvent was used successfully by the authors. Tests with known mixtures of water and toluene show that an additive correction of 0.11 ml. should be made to the water obtained in the distillation of the tar-water mixture.

The recovery train used in this method does not remove

Table III. Duplicate Determinations for 23 Coals Carbonized by Fuel Research Board Assay Test

(As-received basis)

Coal No.	Coke %	Coke Diff.	Tar %	Tar Diff.	Water (Liquor) %	Water (Liquor) Diff.	Gas, by Difference[a] %	Gas, by Difference[a] Diff.	NH_3 (Free Plus Combined) %	NH_3 (Free Plus Combined) Diff.	Gas, as Measured[b] (Air-Free) Cu. ft./ton coal	Gas, as Measured[b] (Air-Free) Diff.	Gross Heating Value of Gas B. t. u./lb. coal	Gross Heating Value of Gas Diff.
1W	69.3	0.3	6.4	0.4	7.5	0.2	[c]	...	0.273	0.013	[c]	...	[c]	...
	69.6		6.0		7.7		[c]		0.260		[c]		[c]	
2	68.2	0.1	5.1	0.0	8.3	0.4	18.0	0.2	0.270	0.006	10,340	200	3320	10
	68.3		5.1		7.9		18.2		0.264		10,140		3310	
3	69.3	0.1	5.9	0.1	7.2	0.4	17.0	0.1	0.271	0.032	10,840	10	3370	10
	69.4		6.0		6.8		17.1		0.303		10,850		3380	
4	79.2	0.3	3.3	0.1	4.6	0.6	12.1	0.3	0.238	0.033	9,890	120	2720	10
	78.9		3.2		5.2		11.8		0.205		9,770		2730	
5	75.4	0.1	3.6	0.8	6.5	0.2	13.8	0.6	0.238	0.001	10,140	90	2860	20
	75.3		4.4		6.3		13.2		0.239		10,050		2880	
6	72.5	0.4	5.6	0.3	7.4	0.0	14.1	0.1	0.239	0.042	10,480	60	2940	50
	72.1		5.9		7.4		14.2		0.197		10,420		2990	
7	75.0	0.4	5.6	0.1	6.0	0.3	12.7	0.6	0.291	0.003	9,490	180	2810	10
	74.6		5.7		5.7		13.3		0.288		9,310		2820	
8	72.9	0.1	5.0	0.1	8.4	0.1	13.1	0.3	0.262	0.005	9.980	340	2970	30
	72.8		4.9		8.3		13.4		0.257		9,640		2940	
9	71.4	0.5	6.7	0.4	6.0	0.2	15.1	0.8	0.195	0.036	9,520	80	3100	90
	70.9		6.3		6.2		15.9		0.159		9,440		3010	
10	65.7	0.0	5.2	0.1	12.9	0.2	15.4	0.0	0.286	0.015	8,770	110	2510	20
	65.7		5.1		13.1		15.4		0.271		8,880		2490	
11	74.8	0.4	4.2	0.2	6.1	0.0	14.4	0.4	0.188	0.091	10,150	50	3090	80
	74.4		4.4		6.1		14.8		0.097		10,200		3010	
12	72.2	0.2	7.4	0.1	4.9	0.3	14.6	0.0	0.146	0.021	10,040	100	3140	20
	72.0		7.3		5.2		14.6		0.125		9,940		3160	
13	68.1	0.0	6.4	0.1	8.1	0.3	[a]	...	0.157	0.014	10,670	80	[c]	...
	68.1		6.5		8.4		16.1		0.143		10,750		3410	
14	68.9	0.5	6.2	0.3	7.6	0.0	16.7	0.8	0.155	0.046	11,170	20	3560	10
	69.4		6.5		7.6		15.9		0.109		11,190		3570	
15	66.8	0.2	6.7	0.3	9.4	0.2	16.3	0.1	0.328	0.011	10,770	120	3430	20
	66.6		7.0		9.2		16.4		0.317		10,890		3450	
16	66.6	0.2	7.5	0.1	8.5	0.0	15.9	0.2	0.233	0.007	9,980	110	3260	30
	66.8		7.4		8.5		15.7		0.226		10,090		3290	
17	72.7	0.3	5.3	0.0	7.2	0.1	13.9	0.4	0.237	0.007	9,920	220	3090	40
	73.0		5.3		7.3		13.5		0.230		10,140		3130	
18	70.4	0.4	5.4	0.0	8.8	0.2	14.7	0.7	0.298	0.018	10,570	200	3260	40
	70.8		5.4		9.0		14.0		0.280		10,370		3220	
19	62.4	0.3	7.0	0.1	12.1	0.2	17.5	0.6	0.378	0.022	9,870	80	3210	110
	62.1		6.9		11.9		18.1		0.356		9,950		3320	
20	68.2	0.1	7.3	0.3	8.2	0.1	15.4	0.1	0.240	0.007	10,240	90	[c]	...
	68.1		7.6		8.1		15.3		0.233		10,150		3230	
21	62.4	0.1	5.5	0.0	17.3	0.2	13.8	0.2	0.357	0.003	8,810	10	2690	30
	62.3		5.5		17.1		14.0		0.354		8,820		2660	
22	68.8	0.1	7.6	0.2	7.8	0.2	15.2	0.1	0.296	0.019	9,950	20	3290	30
	68.7		7.8		7.6		15.3		0.315		9,970		3320	
23	85.1	0.1	1.5	0.0	3.5	0.2	9.6	0.1	0.232	0.006	9,990	90	2660	20
	85.2		1.5		3.3		9.7		0.226		10,030		2680	
Av. difference		0.2		0.2		0.2		0.3		0.020		100		30
Max. difference		0.5		0.8		0.6		0.8		0.091		340		110

[a] H_2S-free; CO_2 included; not scrubbed for light oil.
[b] H_2S-free; CO_2 included; not scrubbed for light oil. Saturated with water vapor at 60° F. and 30 inches Hg.
[c] Not determined.

light oil, carbon dioxide, or hydrogen sulfide from the gas. These are removed from the gas in the recovery train of the United States Steel Corporation method.

Fischer Low-Temperature Assay

Fifty grams of air-dry coal, passing a No. 20 sieve, are carbonized at temperatures gradually increasing to 500° C. in a Fischer cast-aluminum retort (*5*) of 50-gram capacity without the use of superheated steam. With strongly swelling coals, 30- or 40-gram samples are used. The retort was purchased from Andreas Hofer, Mülheim-Ruhr, Germany. It is provided with a high-temperature thermometer and is heated by means of a Meker burner. An asbestos shield, open at the bottom, is placed around the retort to prevent loss of heat.

A 200-ml. Erlenmeyer flask with a 5-cm. (2-inch) side tube is connected to the outlet tube of the retort. This flask, immersed in ice water, collects the tar and water. A 10-cm. (4-inch) glass-stoppered U-tube containing anhydrous calcium chloride is connected to the side tube of the tar-water receiver to remove any water not condensed in the Erlenmeyer flask. The outlet of the U-tube is attached to a freezing tube (*8*) in which the gas is stripped of its light oil. The freezing tube is kept cold (−78° C.) by immersion in a wide-mouthed Dewar flask filled with a thick slush of carbon dioxide snow and acetone.

The gas leaving the freezing tube passes into a calibrated gasometer of 5-liter capacity containing a 20 per cent solution of hydrated sodium sulfate and 5 per cent by volume of sulfuric acid. A manometer is attached to the gasometer. The pressure within the apparatus is maintained at atmospheric during the carbonization of the coal.

After the coal sample is charged into the retort, the retort plug, lubricated with a thin film of graphite and mineral oil to prevent leakage and sticking, is tightly seated in place. The weighed tar-water receiver is attached to the outlet tube of the retort by a cork stopper, so the tube projects 11.25 cm. (4.5 inches) into the Erlenmeyer flask. The cork connection is covered with glycerol-litharge cement to keep the cork from burning and to make a gas-tight joint. The freezing tube, with its stopcocks open, is inserted into the freezing mixture. After the temperature of the freezing tube comes to equilibrium, the stopcocks are closed, the tube is removed and brought to room temperature, and is then dried and weighed. The tube is replaced in the freezing mixture and attached to the U-tube and the gasometer. The apparatus is tested for leaks by putting the system under reduced pressure by means of a leveling bottle attached to the gasometer.

The coal is carbonized at a rate of heating conforming to the time-temperature curve shown in Figure 1. The Meker burner is adjusted to give a long flame and the rate of heating controlled by changing the rate of flow of gas through the burner. The temperature of the retort is raised to a maximum of 500° C. in about 50 minutes. The heating is continued at 500° C. until the gas evolution is not more than 25 ml. per 10 minutes. The total heating time varies from 2 to 3 hours with different coals.

At the end of the carbonization, the stopcocks on the gasometer are closed and the tar-water receiver and the freezing tube disconnected. The gas volume is read and corrected to standard conditions of 60° F. and 30 inches of mercury, saturated with water. A known volume of the gas is bubbled through 1 to 1 potassium hydroxide solution and the hydrogen sulfide determined. A sample of the gas is analyzed in the Bureau of Mines

Table IV. Duplicate Determinations for 20 Coals Carbonized by Fischer Low-Temperature Assay Test

(As-received basis)

Coal No.	Coke %	Coke Diff.	Tar %	Tar Diff.	Water (Liquor) %	Water (Liquor) Diff.	Light Oil %	Light Oil Diff.	Gas, by Difference[a] %	Gas, by Difference[a] Diff.	Gas, as Measured[b] (Air-Free) Cu. ft./ton coal	Gas, as Measured[b] (Air-Free) Diff.	Gross Heating Value B. t. u./lb. coal	Gross Heating Value Diff.
11	82.38	0.22	7.99	0.26	3.38	0.20	0.72	0.02	5.46	0.29	2240	10	1030	0
	82.60		8.25		3.18		0.74		5.17		2250		1030	
12	76.28	0.27	13.19	0.30	4.02	0.13	0.78	0.05	5.49	0.11	1890	60	1000	10
	76.01		13.49		4.15		0.73		5.38		1950		1010	
13	73.08	0.28	12.69	0.50	7.75	0.18	0.83	0.04	5.33	0.97	2070	10	1000	10
	73.36		13.19		7.93		0.79		4.36		2060		1010	
14	74.61	0.60	14.33	0.43	6.55	0.20	0.88	0.08	3.42	0.45	2270	90	1080	10
	74.01		14.76		6.35		0.80		3.87		2180		1090	
15	71.90	0.27	15.65	0.13	6.00	0.25	0.95	0.05	5.35	0.17	2170	10	1050	0
	71.63		15.78		6.25		1.00		5.18		2180		1050	
16	72.26	0.07	15.36	0.03	5.58	0.10	1.15	0.02	5.12	0.16	1950	0	990	40
	72.19		15.39		5.48		1.13		5.28		1950		950	
17	79.10	0.09	10.96	0.11	4.58	0.20	0.66	0.05	4.46	0.06	1990	10	1000	10
	79.19		11.07		4.38		0.71		4.40		1980		1010	
18	76.62	0.05	11.85	0.00	5.60	0.04	0.94	0.02	4.83	0.04	2110	30	1010	10
	76.57		11.85		5.64		0.92		4.87		2080		1000	
19	68.15	0.33	15.37	0.16	10.33	0.20	1.10	0.01	4.70	0.28	1950	30	890	0
	68.48		15.53		10.13		1.09		4.42		1920		890	
20	73.07	0.09	13.88	0.01	5.87	0.10	0.83	0.07	6.06	0.10	1950	10	990	20
	72.98		13.89		5.97		0.90		5.96		1960		1010	
21	66.27	0.16	11.96	0.16	16.43	0.10	0.63	0.02	4.18	0.08	1800	20	850	20
	66.43		11.80		16.53		0.65		4.10		1780		830	
22	73.87	0.02	14.40	0.11	6.46	0.08	0.97	0.01	4.15	0.18	2090	20	1040	10
	73.89		14.29		6.38		0.96		4.33		2070		1030	
23	93.23	0.21	2.97	0.01	1.10	0.04	0.38	0.07	2.31	0.09	1690	10	740	10
	93.44		2.96		1.06		0.31		2.22		1700		750	
24	78.32	0.02	12.24	0.00	4.29	0.00	0.80	0.10	4.26	0.07	2030	0	950	20
	78.34		12.24		4.29		0.70		4.33		2030		970	
25	82.29	0.02	8.81	0.12	4.29	0.20	0.62	0.00	3.92	0.34	1870	80	870	30
	82.27		8.69		4.09		0.62		4.26		1790		840	
26	87.75	0.36	5.33	0.11	2.53	0.07	0.40	0.13	3.87	0.28	1970	60	980	30
	87.39		5.22		2.60		0.53		4.15		1910		950	
27	81.88	0.23	8.89	0.07	3.61	0.01	0.59	0.00	4.90	0.30	2110	80	1050	0
	81.65		8.82		3.62		0.59		5.20		2030		1050	
28	75.62	0.22	13.78	0.29	4.94	0.16	1.15	0.47[c]	4.36	0.56	1930	50	980	20
	75.40		14.07		4.78		0.68		4.92		1980		1000	
29	77.38	0.00	12.01	0.18	4.78	0.02	0.61	0.07	5.07	0.14	1990	10	[d]	..
	77.38		11.83		4.76		0.68		5.21		2000		1020	
30	75.72	0.18	13.05	0.21	4.57	0.10	0.73	0.04	5.74	0.02	1970	10	1000	10
	75.90		12.84		4.67		0.69		5.72		1960		990	
Av. difference		0.18		0.16		0.12		0.04		0.23		30		10
Max. difference		0.60		0.50		0.25		0.13		0.97		90		40

[a] H_2S-free; CO_2 included; scrubbed free of light oil.
[b] H_2S-free; CO_2 included; scrubbed free of light oil. Saturated with water vapor at 60° F. and 30 inches Hg.
[c] Not included in average or in maximum difference.
[d] Not determined.

Table V. Check Limits for Duplicate Determinations

(Same coal by the same laboratory)

Yields	U. S. Steel Corp. Test	Fuel Research Board Test	Fischer Low-Temperature Test
Coke, per cent	0.3	0.4	0.4
Tar, per cent	0.3	0.4	0.4
Water, per cent	0.3	0.4	0.2
Light oil, per cent	0.15	..	0.10
Gas, per cent	0.3	0.8	0.5
Free ammonia, per cent	0.010	..	....
Combined ammonia, per cent	0.015	..	....
Total ammonia, per cent	0.010	0.040	....
Gas, cu. ft. per ton of coal	150	200	100
Gross heating value of gas, B. t. u. per lb. of coal	80	90	40

Table VI. Check Determinations by United States Steel Corporation Test

(Two coals by two laboratories)

Yields, Dry Coal	Coal No. 13[a] U. S. Bureau of Mines	Coal No. 13[a] Illinois Steel Co.	Coal No. 13[a] Difference	Coal No. 15[b] U. S. Bureau of Mines	Coal No. 15[b] Illinois Steel Co.	Coal No. 15[b] Difference
Coke, per cent	71.00	71.08	0.08	70.18	69.60	0.58
Tar, per cent	4.79	5.15	0.36	5.35	5.82	0.47
Free ammonia, per cent	0.330	0.350	0.020	0.264	0.280	0.016
Combined ammonia, per cent	0.043	0.031	0.012	0.063	0.047	0.016
Water, per cent	5.85	6.10	0.25	5.44	5.98	0.54
Light oil, per cent	1.60	1.51	0.09	1.74	1.56	0.18
Carbon dioxide, per cent	1.36	1.36	0.00	1.64	1.63	0.01
Hydrogen sulfide, per cent	0.40	0.41	0.01	0.33	0.35	0.02
Wet gas, CO_2- and H_2S-free, cu. ft. per ton of coal	11,020	10,860	160	11,360	11,050	310

[a] Black Creek bed, Empire mine, Empire, Walker County, Ala.
[b] No. 2 gas bed, Point Lick No. 4 mine, Rensford, Kanawha County, W. Va.

Orsat apparatus (*4*). The Erlenmeyer flask containing tar and water is weighed and the water determined by distillation (*1*), using a mixture of 20 per cent benzene and 80 per cent xylene as a solvent. The aluminum retort, stoppered to prevent absorption of moisture by the coke, is cooled to room temperature and the coke removed and weighed. Dry air is passed through the freezing tube before removal from the freezing mixture, the stopcocks are then closed, and the tube is removed and suspended in the air until it reaches room temperature. The increase in weight of the tube is recorded as light oil.

Yields in gallons per ton of coal are calculated by assuming a specific gravity of 1.00 for the tar and 0.76 for the light oil. The calorific value and specific gravity of the gas are calculated from the gas analysis

Duplicability of Tests on the Same Coal

Tables II, III, and IV give the results of duplicate assay determinations for the coals shown in Table I. From these data, the authors believe that a laboratory should have no difficulty in checking duplicate determinations on the same coal within the limits shown in Table V. In general, the results by the United States Steel Corporation method check somewhat better than do those by the Fuel Research Board method especially for total ammonia.

Table VI shows check determinations by two different laboratories on two coals, using the United States Steel Corporation method. These tests were made on duplicate samples of coal crushed to pass a No. 35 sieve. The yields obtained

Table VII. Factors to Convert Yields by U. S. Steel Corporation Distillation Test to Bureau of Mines–American Gas Association Carbonization Results

Coal No.	Coke 900° C.[a]	Coke 1000° C.[a]	Tar 900° C.	Tar 1000° C.	Water (Liquor) 900° C.	Water (Liquor) 1000° C.	$(NH_4)_2SO_4$ 900° C.	$(NH_4)_2SO_4$ 1000° C.	Gas 900° C.	Gas 1000° C.	Light Oil[b] 900° C.	Light Oil[b] 1000° C.
	%	%	%	%	%	%	*Lb./t.*	*Lb./t.*	*Cu. ft./t.*	*Cu. ft./t.*	*Gal./t.*	*Gal./t.*
11	0.985	0.984	1.63	1.44	1.02	0.85	0.91	0.54	0.95	1.12	0.93	0.89
12	0.963	0.970	1.59	1.37	0.88	0.85	0.83	0.55	0.95	1.06	0.88	0.69
13	0.974	0.974	1.50	1.37	0.89	0.82	0.84	0.68	0.95	1.11	0.85	0.77
14	0.966	0.973	1.45	1.26	0.90	0.85	0.87	0.65	0.92	1.02	1.05	1.05
15	0.952	0.952	1.43	1.30	1.07	1.03	0.77	0.60	0.95	1.04	0.96	0.87
16	0 963	0.968	1.47	1.28	0.96	0.76	0.78	0.56	1.01	1.11	1.06	1.04
17	0 977	0.981	1.42	1.16	0.98	0.81	0.86	0.64	1.02	1.16	1.19	0.98
18	0.971	0.975	1.64	1.36	0.90	0.93	0.81	0.70	0.93	1.07	0.84	0.89
19	0.972	0.972	1.37	1.18	0.93	0.79	0.93	0.66	1.00	1.18	1.12	1.00
20	0.962	0.973	1.51	1.32	0.82	0.79	0.83	0.59	0.96	1.11	0.82	0.96
21	0.993	0.997	1.38	1.21	0.85	0.81	0.78	0.59	1.05	1.15	1.20	1.18
22	0.951	0.971	1.48	1.33	0.90	0.85	0.83	0.64	0.97	1.08	1.01	1.08
23	0.995	0.998	0.86	0.93	0.63	0.54	0.84	0.56	1.07	1.21	0.66	0.68
24	0.970	0.975	1.38	1.23	1.10	0.95	0.87	0.72	0.98	1.10	1.19	1.04
25	0.987	1.001	1.33	1.26	0.81	0.79	0.83	0.61	1.02	1.15	0.90	1.01
26	0.974	0.983	1.30	1.30	1.00	0.86	0.88	0.62	0.97	1.11	0.76	0.72
27	0.975	0.981	1.37	1.34	0.84	0.74	0.76	0.53	1.02	1.12	1.07	1.03
28	0.957	0.962	1.60	1.40	1.02	0.91	0.63	0.56	0.98	1.12	1.35	1.30
29	0.972	0.982	1.36	1.13	0.85	0.89	0.70	0.70	1.02	1.13	0.98	0.97
30	0.968	0.974	1.42	1.28	0.96	0 96	0.79	0.57	1.00	1.10	1.22	1.18
Mean	0.971	0.977	1.42	1.27	0.91	0.84	0.82	0.61	0.99	1.11	1.00	0.97
Deviation from mean												
Av.	0.009	0.009	0.11	0.08	0.08	0.07	0.05	0.05	0.03	0.03	0.14	0.13
Max.	0.024	0.025	0.56	0.34	0.28	0.30	0.19	0.11	0.08	0.10	0.35	0.33

[a] BM-AGA carbonization temperature.
[b] Light oil scrubbed from gas plus fraction of tar distilling below 170° C. in BM-AGA test.

Table VIII. Factors to Convert Yields by Fuel Research Board High-Temperature Assay Test to Bureau of Mines–American Gas Association Carbonization Results

Coal No.	Coke 900° C.[a]	Coke 1000° C.[a]	Tar 900° C.	Tar 1000° C.	Water (Liquor) 900° C.	Water (Liquor) 1000° C.	$(NH_4)_2SO_4$ 900° C.	$(NH_4)_2SO_4$ 1000° C.	Gas 900° C.	Gas 1000° C.
	%	%	%	%	%	%	*Lb./t.*	*Lb./t.*	*Cu. ft./t.*	*Cu. ft./t.*
2	0.985	0.990	1.45	1.35	0.79	0.75	0.95	0.83	1.03	1.12
3	0.977	0.980	1.33	1.08	0.74	0.63	0.78	0.78	0.98	1.10
4	0.995	0.995	1.27	1.30	0.76	0.59	0.91	0.91	0.95	1.12
5	0.993	0.988	1.45	1.25	0.78	0.61	0.92	0.46	1.01	1.12
6	0.981	0.992	1.21	1.09	0.72	0.61	1.28	1.02	0.96	1.08
7	1.009	1.013	0.86	0.66	0.64	0.51	0.90	0.51	1.02	1.17
8	0.988	0.988	1.16	1.02	0.74	0.74	0.91	0.48	1.01	1.15
9	0.986	1.001	0.99	0.97	0.84	0.72	1.07	0.86	1.14	1.27
10	0.976	0.970	0.83	0.65	1.09	0.91	0.92	0.60	1.13	1.34
11	1.000	0.999	1.21	1.07	0.87	0.72	1.57	0.93	1.01	1.19
12	0.982	0.989	1.00	0.86	1.00	0.96	2.14	1.41	1.01	1.12
13	0.984	0.984	1.03	0.98	0.94	0.87	2.05	1.66	0.97	1.13
14	0.977	0.984	1.22	1.06	0.87	0.82	2.07	1.53	0.89	0.99
15	0.984	0.984	1.12	1.02	0.83	0.80	0.77	0.59	1.00	1.10
16	1.001	1.007	1.05	0.92	0.91	0.72	0.94	0.68	1.07	1.18
17	1.003	1.007	1.15	0.94	0.79	0.65	1.19	0.89	1.04	1.18
18	0.999	1.003	1.33	1.11	0.72	0.74	0.94	0.82	0.98	1.13
19	0.997	0.997	0.96	0.83	0.88	0.75	0.95	0.66	1.08	1.27
20	0.991	1.003	1.03	0.95	0.76	0.73	1.05	0.75	0.97	1.12
21	0.973	0.976	1.06	0.93	0.90	0.86	0.92	0.70	1.11	1.22
22	0.961	0 981	1.16	1.04	0.86	0.81	0.94	0.72	1.04	1.16
23	1.008	1.011	0.80	0.87	0.44	0.38	0.68	0.46	1.09	1.22
Mean	0.989	0.993	1.13	1.00	0.81	0.72	1.13	0.83	1.02	1.16
Deviation from mean										
Av.	0.010	0.010	0.14	0.13	0.10	0.10	0.32	0.23	0.05	0.06
Max.	0.028	0.023	0.33	0.35	0.37	0.34	1.01	0.83	0.13	0.18

[a] BM-AGA carbonization temperature.

by the two laboratories check well. As would be expected, the differences between the two laboratories for some of the items are greater than the check limits for duplicate determinations by the same laboratory shown in Table V.

Correlation of Tests

Factors were computed to convert the yields of the small-scale laboratory tests into yields as obtained by the BM-AGA carbonization test using charges of 36 to 45 kg. (80 to 100 pounds) of coal carbonized in a cylindrical retort 32.5 cm. (13 inches) in diameter. These factors are shown in Tables VII, VIII, and IX. The two high-temperature tests—those of the United States Steel Corporation and the Fuel Research Board—are correlated with the BM-AGA carbonization tests run at 900° and 1000° C. The Fischer low-temperature test is correlated with the BM-AGA carbonization tests run at 500° and 600° C.

Tables VII, VIII, and IX show the average, or mean, factors for converting the yields of the laboratory tests into yields of the BM-AGA carbonization tests and the average and maximum deviations from the mean. These deviations from the mean show the extent of the errors that might occur in applying average factors to convert results of the small-scale laboratory tests to those of the BM-AGA carbonization test. On the assumption that the BM-AGA carbonization test is indicative of yields that might be obtained in commercial practice, it is apparent from Tables VII, VIII, and IX that commercial yields cannot be predicted accurately from application of average factors to the results of small-scale laboratory tests. It is probable that average factors could be obtained for closely related types of coal and used satisfactorily for predicting yields for similar coals.

Of the two high-temperature assay tests, that of the United States Steel Corporation gives somewhat more consistent correlation with the BM-AGA carbonization tests than does the Fuel Research Board method. This is especially noticeable in case of ammonium sulfate yields. As far as coke is concerned the two tests are equally good.

Literature Cited

(1) Am. Soc. Testing Materials, Standards, Part 2, p. 891 (1933).
(2) Fieldner, A. C., and Davis, J. D., Bur. Mines, *Tech. Monograph* 5, 1934 (in press).

TABLE IX. FACTORS TO CONVERT FISCHER LOW-TEMPERATURE ASSAY YIELDS TO BUREAU OF MINES–AMERICAN GAS ASSOCIATION CARBONIZATION RESULTS

Coal No.	Coke 500° C.[a]	Coke 600° C.[a]	Tar 500° C.	Tar 600° C.	Water (Liquor) 500° C.	Water (Liquor) 600° C.	Gas[b] 500° C.	Gas[b] 600° C.	Light Oil[b,c] 500° C.	Light Oil[b,c] 600° C.
	%	%	%	%	%	%	Cu. ft./t.	Cu. ft./t.	Gal./t.	Gal./t.
1W	1.054	1.004	0.63	0.69	1.31	1.33	..	..	..	..
2	1.072	0.997	0.59	0.61	1.41	1.18	..	..	..	..
3	1.056	0.974	0.56	0.54	1.24	1.54	..	..	..	..
4	1.015	0.966	0.43	0.63	1.22	1.65	..	..	..	..
5	1.022	0.967	0.44	0.61	1.29	1.65	..	..	..	..
6	1.027	0.964	0.56	0.64	1.25	1.64	..	..	..	..
7	1.038	0.985	0.52	0.71	0.78	1.14	..	..	..	..
8	1.025	0.965	0.52	0.72	1.40	1.51	..	..	..	..
9	1.041	0.984	0.71	0.79	1.22	1.26	..	..	..	..
10	1.007	0.958	0.67	0.67	1.13	1.20	..	..	..	..
11	d	0.971	d	0.73	d	1.24	d	1.86	d	1.20
12	d	0.976	d	0.74	d	1.34	d	2.26	d	1.23
13	1.031	0.969	0.74	0.76	0.99	1.09	1.14	2.14	0.86	0.97
14	1.024	0.966	0.71	0.71	1.02	1.20	1.14	2.00	0.93	1.03
15	1.025	0.971	0.71	0.64	1.15	1.30	1.18	2.14	1.22	1.29
16	1.018	0.983	0.73	0.73	1.15	1.40	1.25	2.05	0.88	1.09
17	1.028	0.968	0.69	0.76	1.07	1.27	1.15	2.15	1.04	1.26
18	1.030	0.969	0.66	0.74	1.07	1.20	1.24	2.19	0.76	0.85
19	1.029	0.972	0.72	0.63	1.04	1.13	1.28	2.26	0.92	1.00
20	1.033	0.971	0.75	0.77	0.98	1.22	1.33	2.41	1.01	1.14
21	1.036	0.970	0.63	0.61	0.98	1.02	1.28	2.33	0.96	0.96
22	1.035	0.969	0.72	0.76	0.88	1.11	1.29	2.10	1.15	1.25
23	0.997	0.960	0.53	0.53	1.18	1.55	1.24	2.38	0.65	0.83
24	1.019	0.967	0.66	0.70	0.93	1.44	1.24	2.02	1.18	1 33
25	1.009	0.962	0.72	0.75	0.98	1.12	1.30	2.30	0.78	1.00
26	0.992	0.951	0.66	0.68	1.27	1.58	1.28	2.54	0.55	0.97
27	1.002	0.954	0.69	0.80	0.89	1.36	1.44	2.51	0.60	1.24
28	1.012	0.951	0.76	0.78	1.20	1.43	1.36	2.28	0.90	0.96
29	1.027	0.968	0.71	0.73	1.21	1.40	1.28	2.10	1.10	1 06
30	1.024	0.967	0.75	0.74	1.11	1.46	1.39	2.34	1.16	1.21
Mean	1.026	0.970	0.65	0.70	1.12	1.33	1.27	2.22	0.92	1.09
Deviation from Mean										
Av.	0.012	0.008	0.08	0.06	0.13	0.15	0.06	0.14	0.16	0.13
Max.	0.046	0.034	0.22	0.17	0.34	0.32	0.17	0.36	0.37	0.26

[a] BM-AGA carbonization temperature.
[b] Light oil not scrubbed from gas in Fischer test for coals 1 to 10, inclusive.
[c] Light oil from gas plus fraction of tar distilling below 170° C. in BM-AGA test.
[d] Not determined by BM-AGA test.

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A Rapid Test for Chlorate Ion

A Qualitative and Approximately Quantitative Test Especially Suitable for Work with Plant Extracts

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A RAPID and convenient test for chlorates has been devised that is especially suitable for work with plant extracts. The method has been developed in connection with studies on the toxic action of sodium chlorate on *Ribes L.*, currants, and gooseberries, and should be of value to other workers for the rapid determination of small amounts of chlorates. No clarification is necessary and only a single drop of the unknown solution is needed. The use of the proposed method permits the rapid examination of a large number of samples of plant material with a minimum of laboratory equipment and labor.

The method depends upon the oxidation of ammonium thiocyanate in specially prepared test paper by the chlorate, with the production of a pale lemon-yellow to cadmium-yellow mixture of oxidation products of sulfocyanic acid. The characteristic color is rapidly developed when the test paper is heated in a drying oven at 95° to 105° C. for 5 or more minutes. Poch (*4*) has previously reported this reaction as a suitable qualitative test for chlorate. He added 1 cc. of 0.5 *N* ammonium thiocyanate to 1 cc. of the chlorate solution, evaporated to dryness, and heated to 140° to 150° C., confirming the presence of chlorate by the appearance of an orange-red coloration.

If a constant quantity of ammonium thiocyanate—i. e., segments of prepared test paper—is used under approximately equivalent temperatures, the intensity and shade of yellow at equilibrium depend upon the concentration of the chlorate ion. This procedure, therefore, can be made roughly quantitative by comparing the color of the unknown against a set of known standards.

ANALYTICAL PROCEDURE

PREPARATION OF THIOCYANATE TEST PAPERS. Immerse Whatman No. 1 filter paper of convenient size in 3 *N* ammonium thiocyanate solution made up from C. P. chemical and distilled water. Remove the papers as soon as they are thoroughly impregnated with the thiocyanate and dry them on a cord sus-

pended above a steam radiator, taking care to keep them out of contact with any metal surface. Turn the papers from time to time to prevent uneven distribution of the thiocyanate. It is important to dry the papers with maximum air circulation at a temperature not exceeding 70° C. When dry place test papers in a clean envelope. If protected from light and dust they may be used for qualitative work for several months. It is not necessary to keep the test papers in a desiccator, provided they are dried prior to use.

Test for Chlorate. Dry the test paper at 60° C. for 10 minutes. Cut from this paper a number of small strips which show no discoloration. To these duplicate test strips add one or more drops of the unknown solution. Place the strips of test paper on a clean watch glass and leave for 5 to 30 minutes in a drying oven operating at any temperature over the range 95° to 105° C. A pale lemon-yellow to cadmium-yellow color shows the presence of chlorate. This color is produced over that area of the paper dampened by the drop of unknown solution. (The color nomenclature used in this paper is that of Ridgeway, *5*.)

Chemical Reactions. It is well known that thiocyanate can be readily oxidized or reduced and that chlorate, particularly in acid solution, is an active oxidizing agent. The reduction of chlorate takes place in different steps and at various rates depending upon the reducing agent, temperature, pH of the medium, and light conditions. Essentially, however, the various steps in the reduction of chlorate may be summarized as:

$$2ClO_3^- \longrightarrow Cl_2 + 3O_2 \qquad (1)$$

Thus, in the reduction of chlorate ion, both chlorine and oxygen may be available as active oxidizing agents. In the present test, the heat decomposition reaction with ammonium thiocyanate proceeds as follows:

$$2NaClO_3 + NH_4CNS \longrightarrow 2NaCl + NH_3 + HCNS + 3O_2 \qquad (2)$$

The thiocyanic acid rapidly forms polymers which in turn are converted to the mixture of yellow oxidation products. The composition of this mixture of yellow colored oxidation products depends on the concentration of the solutions employed, temperature, the pH of the medium, and the presence of other constituents.

Sensitivity of Tests

The results given in Table I show that the method gives a definite test for as little as 0.01 mg. per cc. of sodium chlorate, potassium chlorate, or calcium chlorate. Extracts or solutions containing more than 10 mg. per cc. of chlorate are apt to char the test paper if the oven temperature is greater than 95° C.; such solutions should, therefore, be diluted and an aliquot taken for analysis. With concentrations of 1 mg. or more per cc. the entire area of filter paper covered by the drop of test solution is usually a homogeneous color. In concentrations below 1 mg. per cc. the pale yellow color is most noticeable along the circular margin of the drop. The color produced by 1 mg. per cc. is apparent to ocular observation in diffused daylight. For smaller quantities the color may not be apparent to the naked eye unless the paper is held up before a bright light (preferably a bright sky) and viewed by transmitted light.

The color produced varies from a pale lemon yellow (0.01 to 1 mg. per cc.) through a lemon chrome (1 to 10 mg. per cc.) to an orange or cadmium yellow (10 mg. per cc. or over). In making quantitative tests the best gradation of color is obtained over the range of 0.1 to 10.0 mg. per cc. Between 0.1 and 1 mg. per cc. the presence of an additional 0.2 mg. makes an appreciable difference in the intensity of the coloration. Heating should be continued until no further intensification of the color takes place.

Table II presents data covering experiments with Nitella expressed sap and extracts of *R. petiolare* leaves. Fresh Nitella cells were crushed and the expressed sap was freed of suspended solid organic material by filtration. The pale lemon-yellow color of the filtered sap did not prevent the ready detection of sodium chlorate in concentration as low as 0.05 mg. per cc. Tests were run on the Nitella-chlorate mixture at 24-hour intervals to note the disappearance, if any, of chlorate. At the end of 7 days the color test commenced to be indefinite in the 0.05 mg. solution. The color of the hot sodium hydroxide extract of the *R. petiolare* leaves definitely interfered with the detection of chlorate in concentration below 0.5 mg. per cc. On diluting this dark brown extract with ten volumes of water, a light amber-colored solution was obtained which permitted the detection of chlorate in concentration of 0.05 mg. per cc.

Table I. Sensitivity of Thiocyanate Test Papers for Qualitative Determination of Aqueous Chlorates

Solution Tested	Concn. of Chlorate Solution	Oven Temp.	Period in Oven	Result of Test
	Mg./cc.	*° C.*	*Min.*	
Sodium chlorate	0.01,[a] 0.10, 0.12, 0.16, 0.25	98	85	Pale lemon yellow to cadmium yellow. Positive in all cases
	0.50, 1.00	103	15	
	10.00, 100.00	105	5	
Potassium chlorate	0.01,[a] 0.10, 1.00	98	30	Same as sodium chlorate
	10.00	103	5	
Calcium chlorate	0.01,[a] 0.10, 1.00	98	30	Same as sodium chlorate
	10.00	103	5	
Distilled water	Control	98, 100	85, 30	No color
	Control	103, 105	15, 5	No color

[a] Smallest quantity detectable in aqueous solution.

The products formed on the filter paper consisted chiefly of canarine ($H_6C_8N_8S_7O$) and pseudothiocyanic acid ($HC_3N_3S_3$). Tests were also secured showing the presence of small amounts of isoperthiocyanic acid ($H_2C_2N_2S_3$) and hydropseudothiocyanic acid ($H_3C_3N_3S_2O$). Temperatures below 100° C. and a large excess of the thiocyanate favored the formation of canarine, the true dyestuff (soluble in alkalies and alkali borates), at the expense of the other pulverulent orange-yellow nondye (insoluble in alkali). Higher temperatures and a slight excess of thiocyanate favored the production of the nondyes at the expense of canarine. Poch (*4*) worked with aqueous solutions at temperatures of 140° to 150° C. in conducting his test for chlorate, and reported that the orange-red substance was pseudothiocyanic acid.

Isoperthiocyanic acid was identified by tests described by Stokes and Cain (*7*), canarine and pseudothiocyanic acid by data of Goldberg (*1*), and hydropseudothiocyanic acid following a report by Melis (*2*).

Different combinations of oven temperature (95° to 105° C.) and periods of heating (5 to 240 minutes) were used in the tests reported in Tables I and II. Thus, it was found that an oven temperature of 98° to 100° C. with 30 minutes or more of heating represented more favorable conditions for the determination of 1 mg. or less of sodium chlorate than high temperatures and shorter exposure. If chlorate is present in amounts greater than 1 mg. per cc., 5 minutes in the oven at 103° to 105° C. brings out the color most satisfactorily.

In subsequent experiments positive tests for chlorate were obtained from unfiltered and unclarified cold-water extracts of 1-gram samples of roots, stems, leaves, and petioles of *R. petiolare*. These plants had been allowed to stand for vary-

ing periods in dilute sodium chlorate solutions. Extracts made from untreated plants showed no coloration which might have been confused with the chlorate color.

same lot of ammonium thiocyanate and to use extracts of control plants to which known amounts of sodium chlorate have been added.

Table II. Sensitivity of Thiocyanate Test Papers for Qualitative Determination of Aqueous Chlorate in Mixture with Plant Extracts

Nature of Test Solution	Sodium Chlorate Added to Test Solution	Result of Test
	Mg./cc.	
Nitella expressed sap. (Six series at 24-hour intervals)	0.05,[a] 0.50, 5.00	Pale lemon yellow to lemon chrome. Positive in all cases
	Control	No color
R. petiolare leaves macerated in cold water. Filtrate	0.05,[a] 0.50, 1.00, 10.00, 100.00	Pale lemon yellow to cadmium yellow. Positive
	Control	No color
R. petiolare leaves macerated in cold NaOH (6 *N*). Filtrate	1.00, 10.00, 100.00	Buff yellow to antimony yellow. Positive
	Control	Pale pinkish buff. No yellow tinge
R. petiolare leaves macerated in cold HCl (6 *N*). Filtrate	1.00, 10.00, 100.00	Pale lemon yellow to cadmium yellow. Positive
	Control	No color
R. petiolare leaves boiled in NaOH (6 *N*). Filtrate	0.05	Pinkish buff. Indefinite
	0.50	Cream buff. Fair
	5.00, 50.00	Buff yellow to antimony yellow. Positive
	Control	Cinnamon buff. No yellow tinge
R. petiolare leaves boiled in NaOH (6 *N*), filtrate diluted with 10 volumes of distilled water	0.005	Pale cinnamon pink. No yellow tinge
	0.05[a]	Cream buff. Fair
	0.50, 5.00	Pale lemon yellow to lemon chrome. Positive
	Control	Pinkish buff. No yellow tinge

[a] Smallest amount detectable in light green or light brown plant sap.

Effect of Other Chemicals on Test. In the present procedure, yellow colorations, somewhat similar to those described for chlorates, are produced on the test paper by bromates, iodates, peroxides, persulfates, hypohalites, and halogens. Perborates and borates do not interfere. Colored substances such as permanganates and dichromates mask the color of the chlorate test, while salts of iron, cobalt, copper, and molybdenum produce characteristic colors. For example, copper sulfate produces a green-yellow color, cobaltous chloride a pale cerulean blue, and sodium molybdate a magenta which changes in a few hours to a cedar green.

A satisfactory test for 0.1 mg. of chlorate per cc. may be made in sulfuric, nitric, acetic, oxalic, or sodium hydroxide solutions as strong as 0.1 *N*. The test is unsatisfactory, of course, in any solution that is corrosive enough to injure the test paper. Since chlorides are frequently used as diluents of the sodium chlorate sold for weed-killing purposes, the sensitivity of the procedure was tested for acid and alkaline mixtures of sodium chloride and sodium chlorate. It was found that chlorate in concentration of 0.1 mg. per cc. could be readily detected in acid or alkaline solutions containing 100 mg. per cc. of sodium chloride. In testing the applicability of the method for the determination of chlorate in mixture with the ingredients of typical nutrient water cultures comprising nitrate, phosphate, and sulfate, it was found that a definite color was obtained for 0.2 mg. of chlorate. In neutral or nearly neutral medium 0.1 mg. of chlorate per cc. is the limit of sensitivity in the presence of equal or double the amount of cyanide, thiosulfate, and sulfite. Large excesses of thiosulfate and sulfite (10 times) definitely interfered with the detection of 0.1 mg. per cc.

The presence of any appreciable quantity of free iron will tend to mask the light yellow color produced by low concentrations of chlorate. However, extracts made from plants which had been grown on nutrient solution containing iron tartrate did not exhibit this interference. A c. p. grade of ammonium thiocyanate usually contains about 0.0001 per cent of iron. This is sufficient iron to discolor test papers left exposed to the air, but it does not impair their sensitivity, since the pink coloration always disappears when the papers are heated. Indeed, it has been observed that this slight trace of iron accelerates the oxidation of thiocyanate by chlorate. Sharma (*6*) and Patten and Smith (*3*) have made similar observations regarding the role of iron in the oxidation of ammonium thiocyanate. In quantitative work it is advisable to prepare standards from test papers made from the

Summary

A method has been devised for the detection of small amounts of chlorate which is especially suitable for work with plant extracts. Ammonium thiocyanate in test paper is oxidized by the chlorate compound with the production of yellow oxidation products of thiocyanic acid. The yellow coloration can be made roughly quantitative as well as qualitative by comparing the color of the unknown against the color of standard test papers. Under the conditions of the test the oxidation products consist largely of canarine and pseudothiocyanic acid, with small amounts of hydropseudothiocyanic acid and isoperthiocyanic acid. The sensitivity of the test and the influence of other constituents on the accuracy of the method are also discussed. Halogens, bromate, and iodate, hypohalites, persulfates, peroxides, and cupric salts give somewhat the same coloration of the thiocyanate test paper as the chlorates.

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Corrections. In the paper on "Double-Acid Method of Optical Analysis of Beet Products" [Ind. Eng. Chem., Anal. Ed., **6**, 193 (1934)] the following errors occurred:

On page 197 in the last paragraph, sixth line from the bottom, and on page 199, in the fourth line of the next to last paragraph, the density of the hydrochloric acid should be stated as "1.1029" instead of as "1.029." On page 196, in line 6 of the paragraph following Table IV, the specific conductance of the sugar should be stated as "0.26×10^{-5} at 25° C. in a solution containing 25 grams per 100 ml." instead of "0.26."

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Iodine Value of Tung Oil

Effect of Time, Excess of Wijs Reagent, and Temperature

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As a result of research on the quantitative relations of time, excess of Wijs reagent, and temperature to the iodine value of tung oil, it was found that even after 12 days of contact the iodine value tends to increase. It is proportional to the excess of iodine in centigrams of equivalent iodine per gram of oil, instead of being proportional to the percentage excess of Wijs solution, as usually stated.

If the ratio of Wijs solution added and weight of sample of oil is kept constant, almost identical iodine values are obtained when temperature and time are the same. When time of contact and excess of iodine are constant, the iodine value increases with increase in temperature. With the same excess of Wijs solution, almost identical iodine values can be obtained at different temperatures by varying time of contact.

Standard conditions for converting iodine value are proposed.

It IS well known that iodine values determined by different methods do not agree. Each method has its own merits and drawbacks. The authors have been using the Wijs method in their laboratory and have analyzed about 5000 samples of tung oil during the past 5 years. They have noticed that the ratio of Wijs solution to the weight of oil, the length of time of contact, and the temperature all affect the iodine value. A slight change in any of the above items will cause an appreciable difference in the iodine value.

Up to the present there is no standard specification for the Wijs method. The specifications given by different authorities are tabulated in Table I for comparison.

It is not only impossible to check the iodine value obtained by the Wijs method according to specifications of two different authorities, but also impossible to check the results obtained with the same specification, as variations within the limits are enough to cause an appreciable difference in iodine value.

Table I. Specifications for Determination of Iodine Value Given by Different Authorities

Authority	Concentration of Wijs Solution[a]	Weight of Oil	Temperature	Time of Contact in Dark
	Cg.	*Gram*	*° C.*	*Min.*
Am. Soc. Testing Materials (*2*)	2.6	0.16–0.19	21–23	30
Allen (*1*)	2.6	.....	...	10
Lewkowitsch (*5*)	2.6	0.15–0.18	...	2 to 6 hours
Villavecchia (*6*)	2.6	0.10–0.20	15–18	About 2 hours
Assoc. Official Agr. Chem. (*3*)	2.6	0.10–0.20	...	30
Griffin (*4*)	2.6	0.10–0.20	20–25	1 hour

[a] Equivalent iodine per cubic centimeter.

The purpose of this research is to find the quantitative relations of the different factors with the iodine value of tung oil.

Reagents

Wijs Solution. Dissolve 13 grams of pure iodine in 1 liter of glacial acetic acid (Kahlbaum 99 to 100 per cent) and then pass in chlorine gas, which has been previously dried by passing through two washing bottles, one containing water and the other containing concentrated sulfuric acid. The addition of chlorine gas is stopped when the halogen content is doubled. This solution must be stored in an ice box during the summer and it is better not to use any solution which has been made up more than one month; otherwise the unstable iodine trichloride will be formed and it is not suitable for determining iodine values (*3*, *5*).

Potassium Dichromate Solution. Dissolve 3.8635 grams of c. p. potassium dichromate in water and dilute to 1 liter. One cubic centimeter of this solution is equivalent to 1 cg. of iodine.

Starch Solution. Dissolve 1 gram of soluble starch in 100 cc. of boiling water.

Chloroform. Use pure dry chloroform.

0.1 *N* Sodium Thiosulfate Solution. Dissolve 24.82 grams of pure sodium thiosulfate ($Na_2S_2O_3.5H_2O$) in water and dilute to 1 liter. Let it stand for one month, filter, and standardize by the Volhard method.

General Procedure

Weigh by difference 0.13 to 0.23 gram of oil and put in a 300-cc. iodine flask, add 10 cc. of pure chloroform and then a certain amount of Wijs solution. Place the flask in a thermostat for a definite length of time and, after the flask is taken out, add 10 cc. of 15 per cent potassium iodide solution and 50 cc. of water and titrate with 0.1 *N* sodium thiosulfate solution, using 1 per cent starch solution as indicator. The iodine value is expressed as centigrams of equivalent iodine absorbed by 1 gram of oil.

Effect of Time

The Wijs solution used by the authors contains about 2.6 cg. of equivalent iodine per cubic centimeter of solution, and 25 cc. of Wijs solution is used for every 0.175 gram of oil. When the weight of oil is not exactly 0.175 gram, the amount of Wijs solution is adjusted to this ratio. Reagents are kept at room temperature, while the length of time of contact varies from 0.5 hour to 12 days. The data are tabulated in Table II.

Table II. Effect of Time on Iodine Value

Time of Contact	Average Iodine Value	Time of Contact	Average Iodine Value
Hours		*Days*	
0.5	166.8	1	180.7
2	171.8	2	183.4
4	173.9	6	192.9
7	177.3	10	197.0
		12	199.6

The iodine value increases with the increase in time of contact and, at the end of 12 days, is 199.6. This value is much higher than any given in reference books and will continue to increase if the time of contact is lengthened. It may be possible to reach an end, but it takes too long a time.

Effect of Excess of Iodine

The excess of Wijs solution is usually expressed in percentage. Most reference books state that the iodine value is usually directly proportional to the percentage excess of

Wijs solution, but this statement is not strictly true. It is clearly seen in Table III that samples 1 to 5 have different ratios of Wijs solution and also different iodine values, though the percentage excess is practically the same. From Table III it appears that the iodine value is proportional to the excess of Wijs solution only when the percentage excess is above 39. If we add still less of Wijs solution, the percentage excess will remain around 39, but the iodine value will become considerably lower. If, however, the excess is expressed in centigrams of equivalent iodine per gram of oil, the iodine value will then be proportional (Table IV).

Table III. Effect of Excess of Iodine on Iodine Value

(1 hour at 21.5° C.)

Sample No.	Weight of Oil	Ratio of Wijs Solution to Oil	Excess of Wijs Solution	Iodine Value
	Gram	*Cc./gram*	%	
1	0.2153	11.1/0.13	38.7	123.3
2	0.2090	11.8/0.13	37.8	133.1
3	0.2109	12.5/0.13	37.0	143.4
4	0.1985	13.7/0.13	37.2	156.9
5	0.2282	14.4/0.13	38.8	160.3
6	0.1785	16.4/0.13	45.1	163.6
7	0.1844	20.0/0.13	54.1	167.1
8	0.1723	26.5/0.13	64.7	170.1

Table IV. Relation of Excess of Iodine to Iodine Value

(1 hour at 21.5° C.)

Sample No.	Weight of Oil	Excess of Wijs Solution	Excess of Iodine	Iodine Value
	Gram	%		
1	0.2153	38.7	77.8	123.3
2	0.2090	37.8	80.9	133.1
3	0.2109	37.0	84.2	143.4
4	0.1985	37.2	92.9	156.9
5	0.2282	38.8	101.6	160.3
6	0.1785	45.1	134.4	163.6
7	0.1844	54.1	197.0	167.1
8	0.1723	64.7	311.8	170.1

If the Wijs solution added and the weight of oil are kept at a constant ratio, we get practically identical iodine values (Table V), when temperature and time are kept the same.

Table V. Iodine Value of Oil with Proportional Amounts of Wijs Solution

(Temperature, 21.5° C.)

Weight of Oil	Iodine Value	Weight of Oil	Iodine Value
Gram		*Gram*	
1 hour		2 hours	
0.1343	167.0	0.1398	174.6
0.1456	167.1	0.1668	174.9
0.1527	167.4	0.1722	174.9
0.1642	167.2	0.1850	174.4
0.1740	167.2	0.1950	174.4
0.1804	167.0	0.2226	174.8
0.1910	167.2		
0.2008	167.1		
0.2142	167.2		

Effect of Temperature

We know that both time (Table II) and excess of iodine (Tables III and IV) affect the iodine value. Now we keep the time at 1 hour and the excess around a definite value and determine the iodine values at different temperatures. The data presented in Table VI show that the iodine value increases with the increase in temperature.

Table VI. Effect of Temperature on Iodine Value

Temperature	Excess of Iodine	Iodine Value
° *C.*	*Cg./gram*	
20.0	218.8	166.5
26.3	210.8	167.8
32.0	223.5	170.1
38.6	216.6	171.9

From the results obtained above, it is clear that the iodine value given by any laboratory, up to the present, is only an approximate figure obtained under a certain set of conditions which, even in the same laboratory, can never be all kept identical at different times. It is therefore necessary to set up arbitrary conditions and consider the iodine value thus obtained as the standard iodine value, so that it will be possible to compare the results obtained in different laboratories.

Relation of Time and Temperature

With the same excess of Wijs solution added, it was possible to get almost identical iodine values at different temperatures by varying the length of time of contact.

Table VII. Effect of Time and Temperature at Definite Excess

Temperature	Excess of Iodine	Iodine Value	Temperature	Excess of Iodine	Iodine Value
° *C.*	*Cg./gram*		° *C.*	*Cg./gram*	
	Series A, 1 hour			Series B, 0.5 hour	
	203.0	166.0		202.3	166.0
	203.2	166.3		201.8	166.3
19.5	204.0	165.7	29.5	201.8	166.2
	203.3	166.0		201.5	166.5
	204.0	165.2		200.4	165.6
	202.9	165.5		200.4	166.0
19.9	202.8	166.0	29.9	201.2	165.2
	202.7	165.4		200.5	165.6
	202.2	166.8		198.7	166.9
	201.6	167.3		199.0	167.1
24.5	202.0	167.1	34.6	199.2	167.0
	201.2	167.5		198.9	167.0
	209.0	166.4		198.1	167.0
	200.7	166.8		199.1	166.3
25.1	200.6	166.8	34.9	199.3	166.3
	201.2	166.7		198.2	167.5
	198.0	168.6		195.0	168.1
	197.7	168.1		195.9	167.6
29.9	198.0	168.1	40.5	195.6	167.5
	198.3	167.7		194.2	168.3

In Table VII the results of two series of experiments are tabulated. The excess of iodine for both series is approximately the same, but for series A the reaction temperature is about 10° lower and the time of contact twice as long. It is noteworthy that the iodine values of the different groups in series A are nearly identical with those of the corresponding groups in series B. It may therefore be assumed that the reaction velocity is approximately doubled with a temperature increase of 10° C.

The relation of time and temperature has been worked out on this assumption with 1 hour at 20° C. as the basis and the result is presented in Table VIII.

Table VIII. Relation of Time and Temperature

Temperature	Reaction Velocity	Time of Contact	Velocity Time
° *C.*		*Hours*	
20	V	1	Constant
30	$2V$	$1/2$	
40	$4V$	$1/4$	
50	$8V$	$1/8$	
..	..	..	
t	$2^{\left(\frac{t-20}{10}\right)}V$	$2^{-\left(\frac{t-20}{10}\right)}$	

From this table we see that the time in hours, H, required for a definite temperature equals $2^{-\left(\frac{t-20}{10}\right)}$:

$$H = 2^{-\left(\frac{t-20}{10}\right)} = 2^{\left(\frac{20-t}{10}\right)}$$

$$\log H = \frac{20-t}{10}\log 2$$

$$= 0.030103 \quad (20 - t) \qquad (1)$$

That is, the iodine value obtained by working at t° C. for a contact of H hours will be approximately the same as that obtained at 20° C. for 1 hour, when the excess of iodine is the same in both cases.

The equivalent time, H, in hours is calculated for various temperatures by Equation 1 with 20° C. and 1 hour as the basis. When H is converted into minutes and plotted as shown in Figure 1, it is easy to read the time of contact necessary for any given temperature.

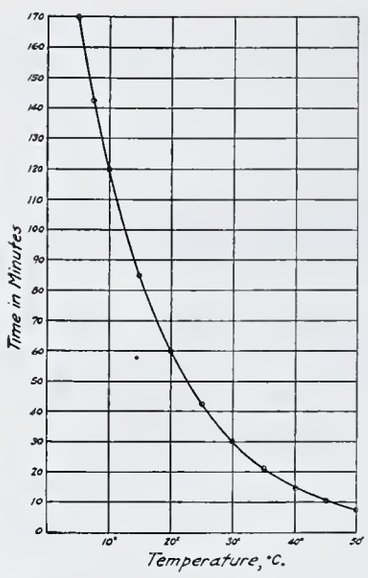

FIGURE 1. RELATION OF TIME AND TEMPERATURE AT DEFINITE EXCESS OF IODINE

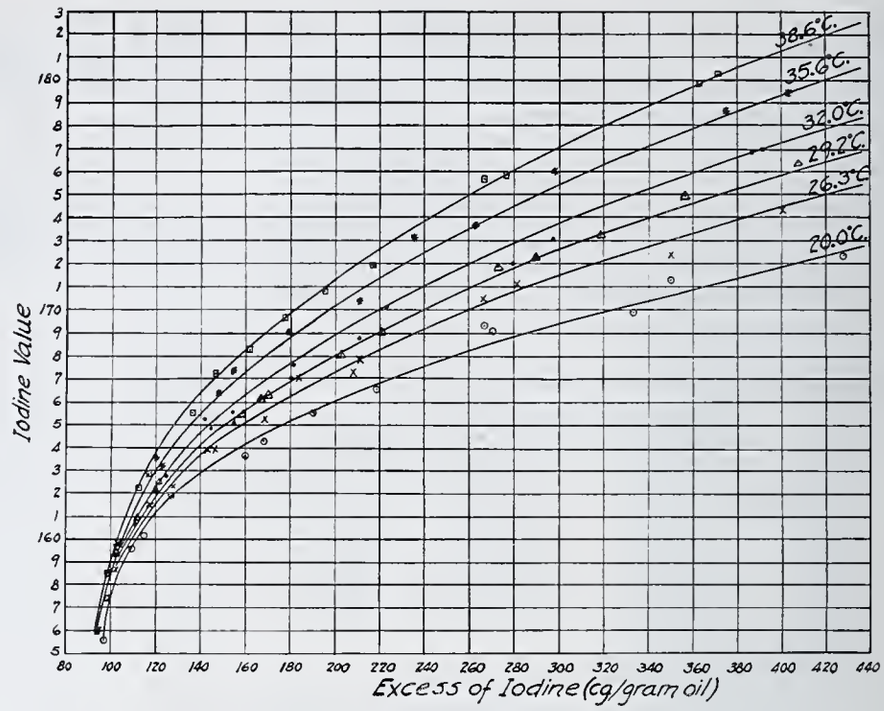

FIGURE 2. IODINE VALUE *vs.* EXCESS AT DIFFERENT TEMPERATURES

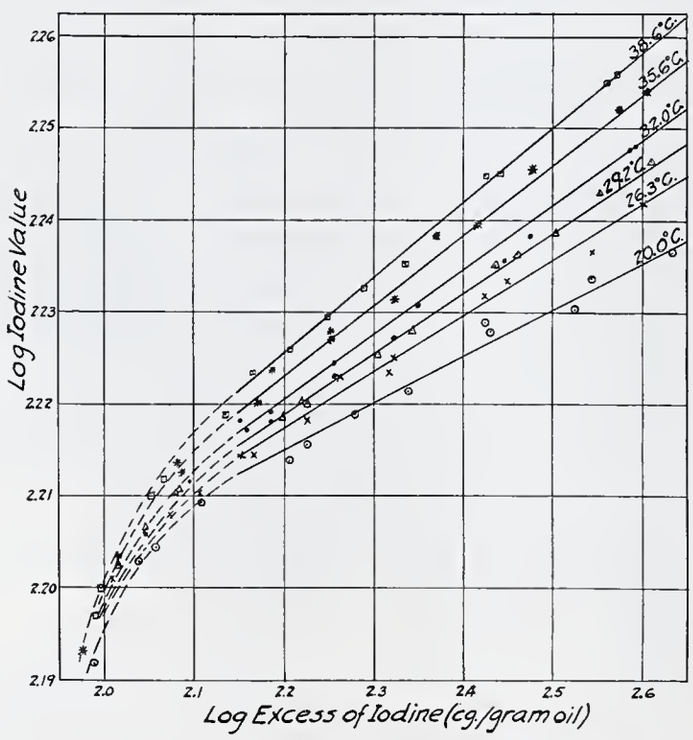

FIGURE 3. LOG IODINE VALUE *vs.* LOG EXCESS AT DIFFERENT TEMPERATURES

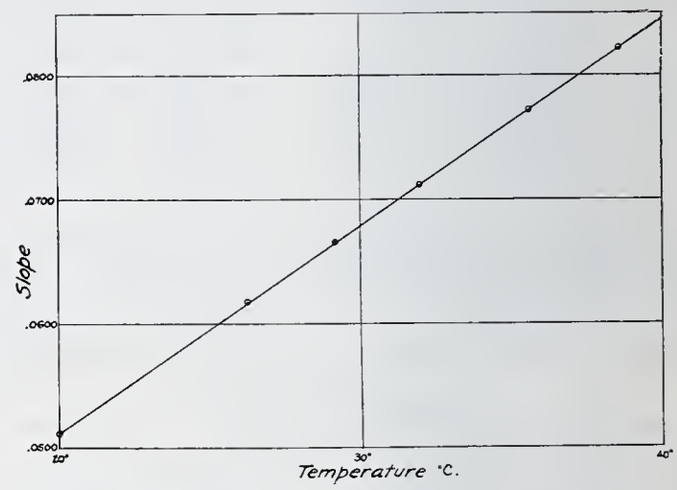

FIGURE 4. SLOPE OF LOG CURVE *vs.* TEMPERATURE

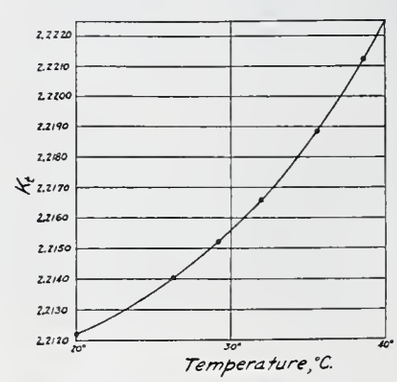

FIGURE 5. K_t *vs.* TEMPERATURE

In order to verify this relation, a series of experiments has been carried out with temperatures and their corresponding time read off from Figure 1. The iodine values thus obtained turn out to be practically the same (Table IX), and prove the validity of Equation 1.

EFFECT OF TEMPERATURE AND EXCESS OF IODINE

It is easy to adjust the time according to the temperature and obtain identical iodine values, but rather inconvenient to add proportional amounts of Wijs solution to oil samples of different weights. It is desirable to find some definite relation of temperature and excess of iodine with the iodine value, in order to determine the iodine value with certain excess of iodine at room temperature and convert to any fixed excess of iodine and fixed temperature chosen as standard. In order to keep the Wijs solution at the same temperature, an automatic buret is used in the same thermostat. The oil is weighed by difference into an iodine flask, chloroform added, and then placed in the thermostat. After both have attained the temperature of the thermostat, the Wijs solution in the automatic buret is then added to the iodine flask. The flask is taken out after exactly 1 hour and titrated in the usual way. The result is given in Table X.

The data in Table X are plotted in Figure 2 with excess of Wijs solution expressed in centigrams of equivalent iodine per gram of oil as abscissa and iodine value as ordinate. From the curves it is clear that the iodine value increases with increase in temperature and with increase in excess of

Table IX. Iodine Values at Different Temperatures with Equivalent Time of Contact

(1 hour at 20° C. as basis)

Temperature	Time	Excess of Wijs Solution	Excess of Iodine Average Value	Iodine Value
° C.	Min.	%	Cg./gram	
		54.92		166.5
17.3	74	54.92	203.9	166.3
		54.92		166.4
		Av. 54.92		Av. 166.4
		54.88		166.4
20.2	59	54.90	203.6	166.5
		54.86		166.4
		Av. 54.88		Av. 166.4
		54.75		166.8
22.3	51	54.79	203.2	166.8
		54.79		166.8
		Av. 54.77		Av. 166.8
		54.84		166.3
25.1	42	54.79	203.1	166.5
		54.86		166.0
		Av. 54.83		Av. 166.3
		54.57		166.4
27.7	36	54.52	201.0	166.6
		54.54		166.5
		Av. 54.54		Av. 166.5
		54.29		166.9
30.4	29	54.39	199.6	166.7
		54.31		166.9
		Av. 54.33		Av. 166.8
		54.17		166.8
36.1	20	54.20	198.3	166.8
		54.13		166.8
		Av. 54.17		Av. 166.8
		54.17		166.6
		54.07		167.0
38.0	17	54.04	197.7	166.8
		54.08		166.8
		Av. 54.09		Av. 166.8

iodine, when the concentration of Wijs solution and the time are kept the same for the different series.

Since no general relation can be deduced from Figure 2, the logarithms of all the values are plotted in Figure 3. All six curves then give fairly straight lines for abscissas 2.15 to 2.65.

Now, if we let m_t be the slope of the line at $t°$ C., the iodine value, Y_t, at excess X can be expressed by the following equation:

$$\log Y_t = m_t (\log X - 2.15) + K_t \qquad (2)$$

where Y_t = iodine value at $t°$ C.
X = excess in centigrams of equivalent iodine per gram of oil
K_t = logarithm of iodine value at $t°$ C. and excess of 2.15

In order to solve Equation 2 we must know definitely the relation between the slope and the temperature. Let us read off in Figure 3 the slopes of the different lines and tabulate in Table XI.

The slope is then plotted against the temperature in Figure 4. It is apparent that

$$\Delta m = \frac{m_2 - m_1}{t_2 - t_1} = \frac{0.08220 - 0.05110}{38.6 - 20.0} = \frac{0.03110}{18.6} = 0.001672/° \text{ C.}$$

where Δm = increment of slope against temperature

But $$\frac{m_t - m_{20°}}{t - 20°} = \frac{m_t - 0.05110}{t - 20} = \Delta m = 0.001672$$

Therefore, $$m_t = 0.001672\,t + 0.01766$$
$$= 0.001672\,(t + 10.56) \qquad (3)$$

Let us go a step further and find out the relation of K_t to the temperature in Equation 2. Read off from Figure 3 and tabulate the results in Table XII.

The values in Table XII are then plotted in Figure 5.

If we subtract from each a common value, B, we get the relation given in Table XIII.

Table X. Relation of Excess of Iodine and Iodine Value at Different Temperatures

(Time of contact, 1 hour)

Concn. Wijs Solution	Excess of Iodine	Iodine Value	Concn. Wijs Solution	Excess of Iodine	Iodine Value
Cg./cc.	Cg./gram	Cg./gram	Cg./cc.	Cg./gram	Cg./gram
	20.0° C.			32.0° C.	
	333.4	169.9		124.6	162.7
	109.7	159.5		386.5	176.9
	266.8	169.3		297.5	173.1
2.549	191.2	165.5	2.532	223.5	170.1
	160.2	163.6		181.2	167.6
	127.3	161.9		154.2	165.5
	...	...		144.6	164.8
	97.5	155.5		391.5	177.0
	114.7	160.1		279.6	172.0
	168.2	164.2		211.2	168.7
2.548	218.8	166.5	2.530	181.0	167.0
	270.0	169.0		154.1	165.1
	350.0	171.3		111.2	160.6
	428.0	172.4		142.0	165.2
	26.3° C.			35.6° C.	
	400.1	174.4		403.0	179.5
	281.6	171.1		298.7	176.0
	169.0	165.2		236.0	173.1
2.546	146.3	163.8	2.524	179.4	169.0
	128.1	162.2		103.8	159.7
	102.5	158.8		120.8	163.5
	...	...		154.7	167.3
	350.4	172.4		375.5	178.7
	266.5	170.5		263.0	173.6
	208.3	167.2		211.5	170.3
2.544	183.7	167.0	2.523	94.9	156.0
	142.5	163.8		122.6	163.1
	117.6	161.4		148.7	166.3
	210.8	167.8		...	...
	29.2° C.			38.6° C.	
	357.2	175.0		363.0	179.9
	289.8	172.3		98.3	157.4
	104.3	159.5		267.0	175.7
2.537	221.0	169.0	2.516	195.4	170.8
	158.3	165.4		161.4	168.2
	111.7	160.9		136.7	165.5
	169.2	166.2		112.5	162.2
	408.0	176.4		371.6	180.3
	318.8	173.3		276.8	175.8
	273.4	171.8		216.6	171.9
2.600	202.3	168.0	2.516	177.7	169.6
	121.5	162.4		99.0	158.5
	166.6	166.1		116.7	162.8
	120.2	162.2		147.0	167.2

Table XI. Relation of Slope and Temperature

Temperature	Slope $m = y_2 - y_1/x_2 - x_1$
° C.	
20.0	$\frac{2.23770 - 2.21215}{2.65 - 2.15} = \frac{0.02555}{0.50} = 0.05110$
26.3	$\frac{2.24486 - 2.21404}{2.65 - 2.15} = \frac{0.03082}{0.50} = 0.06164$
29.2	$\frac{2.24847 - 2.21523}{2.65 - 2.15} = \frac{0.03324}{0.50} = 0.06648$
32.0	$\frac{2.25221 - 2.21663}{2.65 - 2.15} = \frac{0.03558}{0.50} = 0.07116$
35.6	$\frac{2.25746 - 2.21887}{2.65 - 2.15} = \frac{0.03859}{0.50} = 0.07718$
38.6	$\frac{2.26232 - 2.22122}{2.65 - 2.15} = \frac{0.04110}{0.50} = 0.08220$

Table XII. Relation of K_t and Temperature (1)

Temperature	K_t (at the point where logarithm of excess = 2.15)
° C.	
20.0	2.21215
26.3	2.21404
29.2	2.21523
32.0	2.21663
35.6	2.21887
38.6	2.22122

Table XIII. Relation of K_t and Temperature (2)

Temperature	K_t	Common Value, B	$K_t - B$
° C.			
20.0	2.21215	2.20870	0.00345 (= 1 × 0.00345)
30.0	2.21560	2.20870	0.00690 (= 2 × 0.00345)
40.0	2.22250	2.20870	0.01380 (= 4 × 0.00345)
..	.....	2.20870	.....
t	$2^{\left(\frac{t-20}{10}\right)} \times 0.00345 + B$		B $2^{\left(\frac{t-20}{10}\right)} \times 0.00345$

From Table XIII we see that

$$K_t = 2^{\left(\frac{t-20}{10}\right)} \times 0.00345 + B$$

Table XIV. Comparison of Experimental and Calculated Iodine Values

Temperature ° C.	Excess of Iodine Cg./gram	Iodine Value Experimental	Iodine Value Calculated	Difference
	160.2	163.6	164.0	0.4
	168.2	164.2	164.4	0.2
	191.2	165.5	165.5	0
	218.8	166.5	166.7	0.2
20.0	266.8	169.3	168.4	0.9
	270.0	169.0	168.5	0.5
	333.4	169.9	170.3	0.4
	350.0	171.3	170.7	0.6
	428.0	172.4	172.5	0.1
	142.5	163.8	163.8	0
	146.3	163.8	164.1	0.3
	169.0	165.2	165.5	0.3
	183.7	167.0	166.4	0.6
	208.3	167.2	167.7	0.5
26.3	210.8	167.8	167.8	0
	266.5	170.5	170.2	0.3
	281.6	171.1	170.8	0.3
	350.4	172.4	173.1	0.7
	400.1	174.4	174.5	0.1
	158.3	165.4	165.4	0
	166.6	166.1	166.0	0.1
	169.2	166.2	166.1	0.1
	202.3	168.0	168.1	0.1
	221.0	169.0	169.1	0.1
29.2	273.4	171.8	171.6	0.2
	289.8	172.3	172.2	0.1
	318.8	173.3	173.3	0
	357.2	175.0	174.6	0.4
	408.0	176.4	176.1	0.3
	142.0	165.2	164.7	0.5
	144.6	164.8	164.9	0.1
	154.1	165.1	165.7	0.6
	154.2	165.5	165.7	0.2
	181.0	167.0	167.6	0.6
	181.3	167.6	167.6	0
32.0	211.2	168.7	169.4	0.7
	223.5	170.1	170.2	0.1
	279.6	172.0	172.9	0.9
	297.5	173.1	173.6	0.5
	386.5	176.9	176.9	0
	391.5	177.0	177.1	0.1
	148.7	166.3	166.2	0.1
	154.7	167.3	166.7	0.6
	179.4	169.0	168.6	0.4
	211.5	170.3	170.8	0.5
35.6	236.0	173.1	172.2	0.9
	263.0	173.6	173.7	0.1
	298.7	176.0	175.4	0.6
	375.5	178.7	178.5	0.2
	403.0	179.5	179.5	0
	147.0	167.2	167.0	0.2
	161.4	168.2	168.3	0.1
	177.7	169.6	169.6	0
	195.4	170.8	170.9	0.1
38.6	216.6	171.9	172.4	0.5
	267.0	175.7	175.4	0.3
	276.8	175.8	175.9	0.1
	363.0	179.9	179.9	0
	371.6	180.3	180.2	0.1

$$= 2^{\left(\frac{t}{10}\right)} \times 2^{-2} \times 0.00345 + B$$

$$= 2^{\left(\frac{t}{10}\right)} \times 0.0008625 + B \qquad (4)$$

Substituting Equations 3 and 4 in Equation 2, we get

$$\log Y_t = 0.001672\,(t + 10.56)\,(\log X - 2.15) + 2^{\left(\frac{t}{10}\right)} \times 0.0008625 + B \qquad (5)$$

By using Equation 5 it is possible to calculate the iodine value at definite excess (logarithm of which is from 2.15 to 2.65) and temperature (18° to 40° C.) with data obtained at some other excess and temperature within the same limits as above. The time of contact is fixed at 1 hour.

In utilizing Equation 5, B is first calculated by substituting the experimental data in their respective places. The value of B thus obtained is used in the original equation to calculate the iodine value at some desired temperature and excess within limits. The value of B, though slightly different for tung oils having different iodine values, always remains the same for the same sample of oil under different temperatures and excess.

B is calculated by Equation 5 for each iodine value determination in Table X. Among the values thus obtained, there are slight deviations due to inherent experimental errors, but the average is 2.20870, which checks with the deduced value in Table XIII. Using this average value of B, the iodine values at the experimental conditions are then calculated by Equation 5 and tabulated together with the experimental iodine values in Table XIV.

A glance at Table XIV will show that the iodine values obtained from experiments and the corresponding calculated iodine values check rather closely except in a few cases. The deviation in each of those cases is still within 1.

With the help of Equation 5, the iodine value determined under the conditions of any laboratory can be converted to the conditions of other laboratories for comparison. But

Table XV. Iodine Value at Proposed Standard Conditions

Experimental Data: Excess of iodine Cg./gram	Experimental Data: Iodine value	Calculated Iodine Value[a]	Deviation from Average
20.0° C.			
160.2	163.6	167.4	−0.4
168.2	164.2	167.6	−0.2
191.2	165.5	167.8	0
218.8	166.5	167.6	−0.2
266.8	169.3	168.7	+0.9
270.0	169.0	168.3	+0.5
333.4	169.9	167.4	−0.4
350.0	171.3	168.4	+0.6
428.0	172.4	167.7	−0.1
26.3° C.			
142.5	163.8	167.8	0
146.3	163.8	167.5	−0.3
169.0	165.2	167.5	−0.3
183.7	167.0	168.4	+0.6
208.3	167.2	167.3	−0.5
210.8	167.8	167.8	0
266.5	170.5	168.1	+0.3
281.6	171.1	168.1	+0.3
350.4	172.4	167.1	−0.7
400.1	174.4	167.7	−0.1
29.2° C.			
158.3	165.4	167.8	0
166.6	166.1	167.9	+0.1
169.2	166.2	167.9	+0.1
202.3	168.0	167.7	−0.1
221.0	169.0	167.7	−0.1
273.4	171.8	168.0	+0.2
289.8	172.3	167.9	+0.1
318.8	173.3	167.8	0
357.2	175.0	168.2	+0.4
408.0	176.4	168.1	+0.3
32.0° C.			
142.0	165.2	168.3	+0.5
144.6	164.8	167.7	−0.1
154.1	165.1	167.2	−0.6
154.2	165.5	167.6	−0.2
181.0	167.0	167.2	−0.6
181.2	167.6	167.8	0
211.2	168.7	167.1	−0.7
223.5	170.1	167.7	−0.1
279.6	172.0	166.9	−0.9
297.5	173.1	167.3	−0.5
386.5	176.9	167.8	0
391.5	177.0	167.7	−0.1
35.6° C.			
148.7	166.3	167.9	+0.1
154.7	167.3	168.4	+0.6
179.4	169.0	168.2	+0.4
211.5	170.3	167.3	−0.5
236.0	173.1	168.7	+0.9
263.0	173.6	167.7	−0.1
298.7	176.0	168.4	+0.6
375.5	178.7	168.0	+0.2
403.0	179.5	167.8	0
38.6° C.			
147.0	167.2	168.0	+0.2
161.4	168.2	167.7	−0.1
177.7	169.6	167.8	0
195.4	170.8	167.7	−0.1
216.6	171.9	167.3	−0.5
267.0	175.7	168.1	+0.3
276.8	175.8	167.7	−0.1
363.0	179.9	167.8	0
371.6	180.3	167.9	+0.1
		Av. 167.8	

[a] 20° C., 250 cg. excess iodine per gram of oil, 1 hour.

it is desirable for all laboratories to state their iodine values converted to a common set of standard conditions, so that all the results will be uniform and readily comparable without further calculation. The authors therefore propose the following specifications:

Concentration of Wijs solution, 2.5 to 2.6 cg. of equivalent iodine per cc.
Excess of iodine, 250 cg. of equivalent iodine per gram of oil.
Temperature, 20° C.
Time of contact in the dark, 1 hour.
Reagents as given under Reagents above.

Under the proposed conditions, Equation 5 will assume the following form:

log Y (under proposed standard conditions)

$$= 0.001672\,(t + 10.56)\,(\log X - 2.15) + 2^{\left(\frac{t}{10}\right)} \times 0.0008625 + B$$

$$= 0.001672\,(20 + 10.56)\,(\log 250 - 2.15) + 2^{\left(\frac{20}{10}\right)} \times 0.0008625 + B$$

$$= 0.001672\,(20 + 10.56)\,(2.39794 - 2.15) + 2^2 \times 0.0008625 + B$$

$$= 0.001672\,(30.56)\,(0.24794) + 4 \times 0.0008625 + B$$

$$= 0.0161 + B \qquad (6)$$

The individual values of B are separately calculated by substituting the experimental data in Equation 5. The iodine values under the proposed conditions are then calculated by Equation 6, using these individual values of B. The results are tabulated in Table XV.

The iodine values obtained at different temperatures with different amounts of excess of iodine may have a difference of more than 15 in extreme cases, as shown in Table XV. If, however, they are converted to 20° C., 250 cg. excess of iodine, and contact of 1 hour, they give almost the same figure. It is interesting to note that the average value thus obtained is 167.8 and the greatest deviation is only ±0.9.

Conclusions

1. Even after 12 days of contact, the iodine value of tung oil still tends to increase.

2. The iodine value of tung oil is proportional to the excess of iodine in centigrams of equivalent iodine per gram of oil instead of being proportional to the percentage excess of Wijs solution, as usually stated.

3. If the ratio of Wijs solution added and the weight of sample of oil is kept constant, almost identical iodine values are obtained when temperature and time are kept the same.

4. When the time of contact and excess of iodine are both kept constant, iodine value increases with the increase in temperature.

5. With the same excess of Wijs solution, it is possible to get almost identical iodine values at different temperatures by varying the time of contact according to the following relation:

$$\log H \text{ (in hours)} = 0.030103\,(20 - t)$$

6. The following formula is given for converting, within limits, the iodine value to desired conditions with experimental data obtained under laboratory conditions:

$$\log Y_t = 0.001672\,(t + 10.56)\,(\log X - 2.15) + 2^{\left(\frac{t}{10}\right)} \times 0.0008625 + B$$

7. The following conditions are proposed as standard for converting iodine value:

Concentration of Wijs solution, 2.5 to 2.6 cg. of equivalent iodine per cc.
Excess of iodine, 250 cg. of equivalent iodine per gram of oil.
Temperature, 20° C.
Time of contact in the dark, 1 hour.
Reagents as given under Reagents above.

8. The following simplified formula is given for converting the iodine value of tung oil to the proposed standard conditions:

$$\log Y = 0.0161 + B$$

Acknowledgment

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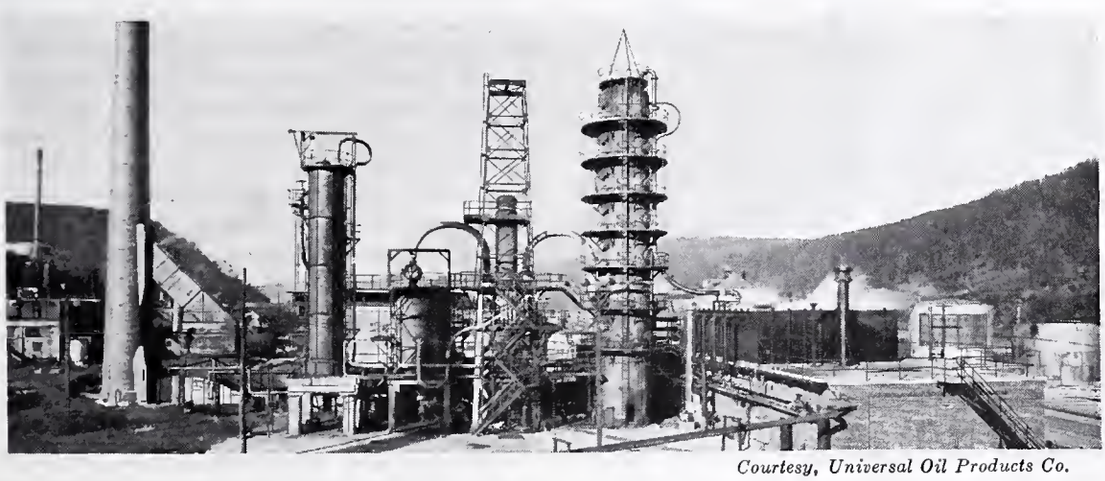

Courtesy, Universal Oil Products Co.

Cracking Unit

Direct Determination of Total Oxygen in Oils

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IN THE process of some experiments on oxidized oils, it became necessary to find a simple means of obtaining their oxygen content which ranged from 0.5 to 15 per cent, usually being about 3 per cent. The problem was to find a satisfactory method to take care of the sulfur and nitrogen, which was about 0.1 per cent, and give good accuracy with such small amounts of oxygen.

The direct determination of oxygen by hydrogenation has been investigated by many chemists (*1, 2, 4, 7–10, 12–16*). For the most part the compounds analyzed contained no elements other than carbon, hydrogen, and oxygen. On the other hand, crude oils contain as much as 2 to 3 per cent of sulfur and nitrogen, depending upon the source (*3*). Upon refining, most of the sulfur and nitrogen is removed, and in highly refined oils, such as cable and transformer oils, the sulfur and nitrogen content runs well below 0.1 per cent.

TABLE I. RUNS MADE WITH TRIONAL

(69.3 mg. of sulfur passed over catalyst before runs were made)

Sulfur Content Taken	Sulfur Content Calculated	Oxygen Found	Oxygen Calculated
Mg.	*Mg.*	%	%
181.2	48.0	26.51	26.41
188.7	49.9	26.00	26.41
201.6	53.2	28.90	26.41
154.2	41.0	26.50	26.41
149.9	39.6	21.00	26.41
		Catalyst inactive	

The ter Meulen method for the direct determination of oxygen in nitrogen-containing compounds has been investigated and modified recently (*13*). The modified method consists of passing the vapors of the organic substance in an atmosphere of hydrogen over a very active thoria-promoted nickel catalyst, thereby converting all oxygen to water which is retained by weighed tubes of sodium hydroxide pellets, while the ammonia gas passes through without being absorbed. When sulfur as well as nitrogen is present, this absorbent cannot be used because hydrogen sulfide is formed and would be retained by the sodium hydroxide. Sulfur also poisons the nickel, probably with the formation of nickel sulfide, gradually destroying the activity of the catalyst (*6, 11*).

TABLE II. RUNS MADE WITH A MIXTURE OF TRIONAL AND SUCCINIC ACID

Sulfur Content Taken	Sulfur Content Calculated	Oxygen Found	Oxygen Calculated
Mg.	*Mg.*	%	%
56.3	2.09	50.40	50.25
63.4	2.20	50.70	50.50
52.8	2.10	49.90	50.00
50.1	2.00	49.80	49.90

WATER ABSORBENT. Calcium sulfate was chosen as being most likely not to absorb either ammonia or hydrogen sulfide, since it is relatively chemically inert (*5*). This desiccant was prepared from plaster of Paris by mixing with water to a paste and heating at 250° C. for 3 hours. It was then crushed, screened to pass four-mesh and be held by ten, and again heated at 250° C. It was tested by passing over it hydrogen sulfide which had first been bubbled through ammonium hydroxide solution. Qualitative tests for ammonia and hydrogen sulfide were negative. Ammonia was tested by odor and by action on litmus, and hydrogen sulfide was tested by alkaline lead acetate. That carbon dioxide was not absorbed was shown by passing this gas over the calcium sulfate and then testing with barium hydroxide.

CATALYST. According to Kelber (*6*), the nickel catalyst can be made more resistant to sulfur by reducing at a higher temperature—namely, 450° instead of 400° C. When this was done, the catalyst remained active in the presence of large amounts of sulfur. In Table I are given the results obtained using trional as a test substance. More than 250 mg. of sulfur were passed over the catalyst before it failed.

About ten analyses can be made without putting in a new charge of catalyst if the sulfur content is no higher than that of refined oils. The carbon should be burned off the cracking surface with air after about 8 grams of oil have passed over it. It is better to oxidize the carbon after each day's work and then reduce the catalyst again overnight. Reduction is complete in 10 hours at the high temperature used. Two to three runs can be made in one day. Upon oxidation the nickel sulfide goes to nickel sulfate which gradually accumulates and finally causes destruction of the catalyst. For this reason the catalyst should be tested periodically with a known compound such as succinic acid.

METHOD AND APPARATUS

The method finally used was the same as that of Russell and Marks (*13*), except that calcium sulfate was used throughout the system to replace the sodium hydroxide pellets, and the catalyst was reduced at 450° instead of 400° C. Reduction of the catalyst at this higher temperature is doubtless in large measure responsible for the low blanks obtained, usually being below 0.1 mg. per 0.5 hour and seldom above 0.3 mg.

TABLE III. ANALYSES OF OXIDIZED OILS

Substance	Taken	Percentage	Average
	Grams		
Run No. 1 oxidized oil	2.1687	2.20	
	2.1252	2.10	2.15
Highly oxidized refrigerator oil	0.2379	11.75	
	0.2084	11.90	
	0.2042	11.89	11.87
	0.1993	11.99	
	0.2430	11.85	
Run No. 11 oxidized oil	1.1533	1.53	1.52
	2.1938	1.51	
Run No. 20 oxidized oil	1.7884	1.50	
	2.0263	1.55	1.515
	1.7924	1.50	

Because of the large combustion tube used (15 mm. inside diameter) special methods were necessary for keeping air out of the system when the sample was introduced. The quartz combustion tube was drawn out at the absorption end and a short length of rubber tubing used for connecting to the first tube. This rubber tube was closed with a pinch-clamp before removing the first absorption tube. Before making a run, the sample was put in and the tube flushed out for 15 minutes, to remove any air which might have entered from that end.

A quartz boat was used in this work, since platinum would be attacked by the sulfur in the oils. The boat was easily cleaned from adhering carbon by heating in an oxygen-hydrogen flame.

In making a run the rate of hydrogenation of the carbon-oxygen compounds was controlled by watching the narrow tube at the absorption end. As soon as water condensed here, heating of the sample was discontinued until this water had passed into the absorption tube.

In the case of oils volatile at around 50° C., it was necessary to introduce them into the heated portion after the

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system had been flushed out without removing the rubber stopper. The boat was put in the cold part of the tube while it was being flushed out, and then pushed into the heating zone by means of a glass rod, running in a glass collar in the rubber stopper at the sample end of the combustion tube. A short piece of rubber tubing, forming an air-tight sleeve between the glass collar and the rod, was found to be especially convenient when successive runs were to be made, because it was not necessary to wait for the sample-heating furnace to cool.

Oil vapors have a tendency to diffuse back into the cool part of the combustion tube and condense on the rubber stopper, ruining the analysis. By very slow heating and close watching of the sample, the diffusion can be reduced to a minimum. The portion of the tube before entering the furnace was made about 15 cm. (6 inches) long, so that any oil diffusing back would condense there and could be flamed out. A clear quartz tube is essential in order that the progress of the heating may be followed. Diffusion could probably be avoided by the use of a plug put in after the boat had been placed in the tube. This would increase the velocity of the hydrogen at that point and therefore retard the oil vapor diffusion, but it seems inconvenient and not necessary if sufficient care is taken in the heating of the sample.

Results

The results obtained are shown in Tables I to III. In order to test the method, several runs were made with mixtures of succinic acid and trional which as aliphatic compounds should rather closely approximate petroleum oils in their behavior. Enough trional was added to make the weight of sulfur the same as would be present in 2 grams of oil containing 0.1 per cent of sulfur. The results are shown in Table II. The accuracy is about that to be expected from this type of method. Analyses made on several types of oxidized oils are presented in Table III. A good reproducibility is evident and as good an accuracy as was obtained with the known compound may be reasonably expected.

The method has given good results with sulfur compounds even when small amounts of oxygen are involved. It is hoped at some later date to deal with still other sulfur compounds using this method of oxygen analysis, as it is believed that it should be of rather general applicability.

Acknowledgment

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Determination of Free Sulfur in Rubber

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The determination of free sulfur in vulcanized rubber has always been an important analytical operation. It has been accomplished in the past by extraction and direct weighing (*2*); by conversion into thiocyanate and titrating with silver nitrate (*2, 3, 8*); by conversion into thiosulfate and titration with iodine (*1*); by reduction with tin, hydrochloric and acetic acid, and titration of the hydrogen sulfide with iodine (*5*); and by oxidation and gravimetric estimation as barium sulfate. Under the last method, oxidizing materials employed have been nitric acid and potassium chlorate (*2*), liquid bromine (*10*), potassium permanganate (*4*), and nitric and perchloric acids with bromine (*7*).

The oxidation and gravimetric methods are on the whole satisfactory, that of Tuttle (*10*) being generally preferred as most convenient. The volumetric methods proposed are all lacking in some essential features, usually arising from slow or incomplete reactions or unsatisfactory end points. The chief objection to the gravimetric methods is in the large amount of time consumed in oxidation, precipitation, digestion, filtration, preparation of crucibles, and weighing. A minor objection is that the oxidation methods do not differentiate between true free sulfur and sulfur in organic compounds which may be present in the acetone extract (*6*).

The volumetric method described below avoids all these objections. It is rapid, accurate, and distinguishes between true free sulfur and organically combined sulfur. It should be useful not only in the rubber laboratory but wherever small amounts of free sulfur must be accurately determined.

Volumetric Method

It was recently observed in this laboratory that when a clean surface of metallic copper is exposed to sulfur dissolved in acetone, the sulfur is quickly and quantitatively absorbed with the formation of a black film of cuprous sulfide. When no interfering substances are dissolved in the acetone in addition to the sulfur, the copper may be weighed before and after reacting with the solution and the sulfur obtained by the difference in weights. However, in the extract of a rubber sample, almost invariably there will be found interfering materials such as the acidic softeners usually employed, certain accelerators and antioxidants, and even the natural resins of the rubber itself. Certain of these are absorbed or react sufficiently with the copper so that high results are obtained by direct weighing. An indirect method, therefore, must be used. Such a method was developed, based on the discovery that hot, concentrated hydrochloric acid attacks and completely removes the film of sulfide from the copper with the quantitative evolution of hydrogen sulfide. The latter is

absorbed and determined by titration with standard iodine or preferably with iodide-iodate solution in a manner similar to the well-known method for sulfur in iron.

The form of copper best suited for this procedure was found to be gauze of about 40 mesh, cut into narrow strips about 0.6 cm. (0.25 inch) in width and 45 cm. (18 inches) long. The strip is then wound about a pencil to form a loose spiral about 2.5 cm. (1 inch) in diameter, which weighs slightly more than 4 grams and has by calculation a surface of more than 65 sq. cm. (10 square inches). One such spiral, cleaned with boiling, concentrated hydrochloric acid, and rinsed with water and acetone, is dropped into each extraction flask with the acetone when the extraction is started. Any form of extraction apparatus may be used, or the rubber sample may be simply boiled under reflux in the acetone with the copper spiral. The sulfur is continuously removed from the solution by the copper until the reaction is complete. The copper spirals may be used for many determinations.

Procedure. The rubber samples are weighed out, wrapped in filter paper, and placed in the siphon cups of the Underwriters' type extraction apparatus. The size of the sample should be regulated according to the probable amount of free sulfur present. For vulcanized, nonblooming tire stocks, samples of 1 to 2 grams are satisfactory. A spiral of clean copper gauze prepared as described is placed in the flask with 50 cc. of acetone and the extraction carried out for 6 to 8 hours. The acetone is then poured off the sulfurized spiral, which is rinsed with one or more portions of fresh, hot solvent until free of soluble resinous materials. If any cuprous sulfide is seen to have scaled off the spiral, the rinsing must be done carefully so that the sulfide particles are retained in the flask with the spiral. The flask and contained spiral are then dried in the oven at 60° to 80° C., and the flask is connected with the gas-evolution apparatus.

This consists of a two-hole rubber stopper, fitted with a thistle and a delivery tube, which is forced tightly into the neck of the extraction flask with the end of the thistle tube extending almost to the bottom of the flask. The delivery tube is connected to a small wash bottle and the latter to a second tube extending about 3.8 cm. (1.5 inches) below the surface of an ammoniacal cadmium chloride solution in a second flask. This solution is conveniently prepared by dissolving 10 grams of cadmium chloride in 200 cc. of water and adding 300 cc. of concentrated ammonium hydroxide solution. Ten cubic centimeters of this solution, diluted as required, are used for each determination.

The gas evolution is accomplished by pouring 20 cc. of concentrated hydrochloric acid through the thistle tube into the flask, and placing the latter on an open hole on the steam bath. The hydrogen sulfide is quickly evolved and carried over with considerable hydrogen chloride through the wash bottle into the absorbing solution. The wash bottle should contain a little concentrated hydrochloric acid which will maintain an approximately constant strength and volume as the hydrogen chloride gas is bubbled through it. After 5 minutes on the steam bath, the apparatus is removed and a gentle stream of air is passed through it for 1 minute to sweep all remaining traces of hydrogen sulfide into the absorbing solution. Care must be exercised to maintain the absorbing solution in an alkaline condition, since too much heat or too prolonged an air treatment may carry so much hydrogen chloride over that the cadmium chloride solution will become acid and no longer absorb the hydrogen sulfide.

The delivery tube is then disconnected from the wash bottle and 0.04 N potassium iodide–iodate solution is measured from a buret into the still alkaline absorption mixture to an estimated slight excess, judging by the amount of cadmium sulfide precipitated. Ten cubic centimeters of concentrated hydrochloric acid are then added all at once and the mixture is shaken. If the color of the iodine disappears, more iodide-iodate solution is added until a permanent yellowish tint is obtained. After about a minute, starch indicator is added and the excess iodine is back-titrated with 0.04 N thiosulfate solution.

To test the accuracy of the method, a prepared solution of 0.2 gram of sulfur in 500 cc. of acetone was used. Six 25-cc. portions of this solution, each containing exactly 0.01 gram of sulfur, were transferred to clean flasks and into each was introduced a prepared spiral of gauze. The flasks and contents were allowed to stand in a warm place overnight, but were not refluxed, since the block tin coils of the rubber extraction apparatus available appeared to be slightly contaminated with sulfur and might have caused high results. In the morning, after testing the acetone with clean copper gauze and finding it to be free of sulfur, it was poured off and after drying the flasks and spirals, the sulfur was determined as described. The sulfur values obtained for the six samples were 0.01007, 0.00995, 0.01010, 0.00990, 0.01007, and 0.00998; average, 0.01001.

To obtain a comparison between the free sulfur values as determined by the new method and by the bromine oxidation-gravimetric procedure, an inner tube stock with a high content of a sulfur-bearing accelerator, mercaptobenzothiazole, was first selected. A considerable number of samples, cut from the same piece of rubber, were tested by the two methods with results shown in Table I.

Table I. Comparative Free Sulfur Values

Sample	Old Method	Sample	New Method
	%		%
1	0.845	7	0.705
2	0.865	8	0.725
3	0.840	9	0.690
4	0.860	10	0.717
5	0.860	11	0.685
6	0.870		
Av.	0.857	Av.	0.704

As was expected, the values obtained by the oxidation method were considerably higher than those by the new procedure, owing to the sulfur in the accelerator, part of which is extractable with acetone.

In connection with routine curing control tests, a considerable number of tires were checked for free sulfur in tread, cushion, and carcass by the new method and by the bromine oxidation-gravimetric method. Results on the first eleven tires are given in Table II.

Table II. Determination of Free Sulfur in Tires

No.	Tread		Cushion		Carcass	
	Old	New	Old	New	Old	New
	%	%	%	%	%	%
1	0.29	0.26	0.67	0.63	0.78	0.73
2	0.32	0.32	0.74	0.72	0.71	0.66
3	0.49	0.48	0.82	0.81	0.83	0.82
4	0.38	0.32	0.61	0.61	0.34	0.29
5	0.11	0.07	0.47	0.51	0.86	0.81
6	0.43	0.41	1.08	1.03	1.16	1.10
7	0.48	0.44	0.58	0.58	0.45	0.39
8	0.27	0.29	0.55	0.57	0.65	0.65
9	0.30	0.27	0.73	0.69	0.74	0.74
10	0.46	0.43	0.84	0.85	0.66	0.65
11	0.58	0.56	0.77	0.68	0.75	0.75

The differences are small, usually well within the range of experimental error for free sulfur determinations, although the values by the new method will average, as would be expected, slightly lower than by the oxidation-gravimetric procedure.

Conclusions

The advantages of the new method for free sulfur may be summarized briefly as follows: (1) it is much faster than previous methods, (2) it is more accurate than older methods in the presence of organic sulfur compounds, and (3) it eliminates bromine or nitric acid fumes in the laboratory and does away with a large amount of equipment in beakers, funnels, crucibles, and filter papers.

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Metallic Salts of Ursolic Acid

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FOR some years past, work has been in progress at this laboratory on the preparation of ursolic acid and other constituents of apple peel. It had been planned to present the results of this work in a series of papers beginning with the preparation of the crude extracts. However, the appearance of a paper on lead ursolate by Cohee and St. John (*1*) has prompted the publication of the following description of a number of salts of ursolic acid.

Previous work on salts of ursolic acid seems to have been fragmentary. Dodge (*2*) reported a crystalline potassium salt of ursolic acid, $C_{30}H_{47}O_3K$, for which he gave an indirect method of analysis. He also described the preparation of an amorphous lead salt and a crystalline zinc salt, and mentioned magnesium and ammonium salts of ursolic acid, but did not report analyses for them. Sando (*5*) prepared sodium ursolate, for which he found the formula $C_{30}H_{47}O_3Na$.

The ursolic acid used in the following preparations was pure material which had been repeatedly recrystallized and exhibited the accepted melting point, 283–84° C. Three grams of its sodium salt were dissolved in 50 per cent alcohol and brought into reaction with a solution of a salt of the metal, the ursolate of which it was desired to prepare. The new salt of ursolic acid formed by double decomposition was filtered on a Büchner funnel, washed successively with water, alcohol, and ether, and dried in air and finally in an Abderhalden drier at 111° C. (vacuum, P_2O_5).

The analyses were conducted in accordance with directions or suggestions given by Treadwell-Hall (*6*) and Kamm (*4*). In the last column in Table I it will be noted that most of the metals were weighed as sulfate. Simple ignition of the silver salt gave, as usual, metallic silver, and the ash residues from the aluminum and nickel salts were regarded as oxides. The observed percentages of metal have been rounded off in the first decimal place, because the nature of these preparations does not warrant the assumption of any greater accuracy, and are tabulated in apposition to the calculated values. The agreement between the observed and the calculated values leaves no doubt that ursolates obtained are the normal salts of the metals, corresponding in each instance to the simple salt which entered into the double decomposition. Other preparative and analytical details are presented in Table I.

Table I. Salts of Ursolic Acid

Salt	Salts Added	Yield	Color	Appearance	Metal Calcd.	Metal Found	Metal Determined as:
	Grams	*Grams*			%	%	
Aluminum ursolate	0.82 $AlCl_3$	1.0	White	Cryst.	1.94	2.0	Al_2O_3
Barium ursolate	1.53 $BaCl_2.2H_2O$	2.6	White	Amor.	13.12	12.8	$BaSO_4$
Calcium ursolate	0.69 $CaCl_2$	1.7	White	Cryst.	4.21	4.0	$CaSO_4$
Cadmium ursolate	1.37 $CdCl_2.2H_2O$	3.0	White	Amor.	10.99	11.1	$CdSO_4$
Cobalt ursolate	1.48 $CoCl_2.6H_2O$	1.7	Purple	Amor.	6.08	5.9	$CoSO_4$
Lead ursolate	2.38 $Pb(Ac)_2.3H_2O$	2.9	White	Cryst.	18.54	18.5	$PbSO_4$
Lithium ursolate	0.26 LiCl	1.2	White	Cryst.	1.50	1.3	Li_2SO_4
Magnesium ursolate	1.28 $MgCl_2.6H_2O$	1.2	White	Cryst.	2.60	2.4	$MgSO_4$
Manganese ursolate[a]	1.24 $MnCl_2.4H_2O$	1.3	Grayish brown	Cryst.	5.69	5.3	$MnSO_4$
Nickel ursolate	1.48 $NiCl_2.6H_2O$	1.7	Grayish green	Amor.	6.06	5.4	NiO
Silver ursolate[a]	1.06 $AgNO_3$	1.3	White	Amor.	19.16	18.7	Ag
Strontium ursolate	1.67 $SrCl_2.6H_2O$	2.5	White	Cryst.	8.77	8.2	$SrSO_4$

[a] Ether wash eliminated in this preparation.

Since their findings differ from the analyses of Cohee and St. John for the lead salt, the authors' figures are given:

0.3149 gram substance	0.0861 gram $PbSO_4$
0.2843 gram substance	0.0765 gram $PbSO_4$
Found, Pb	18.7 and 18.4
$Pb(C_{30}H_{47}O_3)_2$ requires, Pb	18.54

Ursolates of mercury, copper, arsenic, antimony, bismuth, iron, chromium, and zinc have been prepared in an apparently pure state, but the authors are not yet prepared to report the analyses.

Inasmuch as these salts comprised a fair range of metallic elements, it was of interest to learn whether there was a corresponding variation in their solubilities. Qualitative tests indicated that all the salts were insoluble in hexane, and apparently so in glycerol. Ether was a somewhat better solvent. Dioxan, butanol, and butyl acetate were in general the best solvents. Comments on specific differences, of which there appeared to be several instances, are being withheld pending accumulation of more nearly quantitative data.

Reference has been made to the discrepancy between the authors' observations on the composition of lead ursolate and those of Cohee and St. John. The latter added lead acetate to a solution of ursolic acid in ethanol and completed the precipitation by the addition of water. Their product contained 10.51 per cent of lead, which they interpreted to mean that the lead had become tetravalent if the monobasicity of ursolic acid is accepted. This assumption of tetravalent lead did not seem correct. In the first place, the authors had already obtained a normal, bivalent lead salt. Moreover, Dodge (*2*) had pointed out that potassium ursolate hydrolyzes in aqueous media to such an extent that ursolic acid or an acid ursolate is precipitated. Of this phenomenon the authors have had abundant confirmation from their own experience and are of the opinion that the analytical result of Cohee and St. John is due to an unfortunate method of preparation. In their reaction the liberated acetic acid would compete with the ursolic acid for lead, and the addition of water would precipitate any unreacted ursolic acid. Without further appropriate manipulation to purify the precipitate, a normal product could scarcely be obtained.

Apart from analytical considerations, it seems to the authors that Cohee and St. John have been somewhat uncritical in advancing the suggestion that tetravalent lead was present in their lead ursolate. If the preparation of lead tetraäcetate by Hutchinson and Pollard (*3*) may be accepted as a model, a tetravalent lead atom must be present initially. In this latter instance the lead was introduced as Pb_3O_4. Moreover, tetravalent lead is usually unstable, and the simple salts, both inorganic and organic, hydrolyze readily. Hence it would be anticipated that an oxidizing agent would be required to produce a tetravalent ursolate when the lead was introduced as its bivalent acetate, and that aqueous reaction media should be avoided to prevent hydrolysis of any tetravalent salt produced. Neither condition was fulfilled, except as atmospheric oxygen, ordinarily ineffective for this purpose, was not excluded.

Preparation of Lead Salts

To clarify the situation, lead salts were prepared by the following procedures:

Method A. For this preparation 3 grams of ursolic acid were dissolved in 400 cc. of hot 95 per cent alcohol. To this solution were added 2.5 grams of crystalline lead acetate dissolved in 30 cc. of hot water. The hot mixture was set aside to cool gradually and finally placed in a refrigerator. The lead ursolate separated in a crystalline condition and was filtered out on a Büchner funnel. It was washed with water and alcohol, again with water and alcohol, and finally with ether. It was then air-dried overnight before being desiccated in an Abderhalden drier at 111° C.

0.2426 gram substance	0.0650 gram $PbSO_4$
Found, Pb	18.3
$Pb(C_{30}H_{47}O_3)_2$ requires, Pb	18.5

Method B. In this preparation the method as described by Cohee and St. John was literally followed, except that half quantities were used.

0.2032 gram substance	0.0470 gram
Found, Pb	15.8

Method A differs from method B in that a molecular quantity of lead acetate was used and that the product was allowed to separate under conditions favoring crystallization. Furthermore, the product was subsequently treated to eliminate both unreacted lead acetate and ursolic acid. The analytical results confirmed the authors' previous finding. The analytical result for method B, a repetition of the experiment by Cohee and St. John, indicated an impure product, but did not duplicate their finding. Since method A gave an analytically pure product, whereas method B did not, the authors interpret these observations as a confirmation of their criticism.

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Determination of Lactose in Mixed Feed

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A method for the determination of lactose in present-day complex, mixed feed has been developed and shown to be accurate to ±0.25 per cent of lactose. Corrections of blanks and losses have been incorporated.

The method entails no exceptionally specialized laboratory technic.

The application of this method to the determination of dry skim milk percentages in mixed feeds is indicated, and application to other dairy products in mixed feeds is suggested.

The consumption of dry milk products in mixed feeds has shown a phenomenal increase during the 15 to 18 years since the first use of these products by feed manufacturers. This increase has been particularly rapid during the last 5 or 6 years.

It is of interest to feed manufacturers and feed control officials to be able to find out the amount of milk used in so-called milk mashes and other feed mixtures featuring milk as an ingredient. Qualitative methods for the detection of milk in feed mixtures do not give the desired information, and former quantitative methods have not been accurate when applied to the present complex feed mixtures that are on the market.

The literature dealing with the determination of lactose or milk solids in mixed feeds is very limited. Two papers were published in 1928. Coe (*2*) describes a method for the estimation of dried buttermilk from the lactose content of feed, and names cottonseed meal and soy bean meal as interfering with the accuracy of the results obtained by his method.

Davis (*3*) published seven methods to be used in determining the amount of dry buttermilk in feed mixtures. Some of these methods are quantitative and others are qualitative.

Difficulties Caused by Present Feed Mixtures

It has been possible to determine lactose in simple feed mixtures consisting of ground grains, mill feed, certain types of meat scrap, and dairy products, by following some of the methods previously recommended. Present feed mixtures, however, are apt to be exceedingly complicated. It is not out of the ordinary to find mash feeds containing from twelve to twenty different ingredients. Such ingredients include the various ground grains, the common grain by-products produced in the milling of grain, the by-products of corn starch and sugar manufacture, the oil meals resulting from the extraction of oils from various meat products, many kinds of fish meals, whale guano, mineral materials of various sorts, molasses, and sometimes flavoring materials.

The meat packinghouse by-products may be used separately, or may be present in a mixture sold as meat scrap. Evaporated tank water or "stick" is a soluble protein material which is hard to precipitate, but which may be found in connection with tankage or other meat products. The nitrogenous material in the various protein concentrates is not necessarily in combination as protein at all times. Upon partial hydrolysis some of the amino-acid components of proteins are set free, causing difficulty in precipitation.

Some of the oil meals contain sugars which are not fermented by ordinary yeast, but which do reduce copper. It has been necessary to devise an application of enzymes so that such sugars are changed into fermentable form. This must be done without attacking or changing the lactose present.

Method

Apparatus and Reagents. Centrifuge and suitable sediment tubes, and I G 4 Jena fritted-glass filtering crucibles.

Animal diastase (Armour & Co., Pharmaceutical Dept., Chicago, Ill.), invertase-melibiase scales (Wallerstein Laboratories, Wall St., New York, N. Y.), baker's yeast, solution of saturated neutral lead acetate, solution of 5 per cent mercuric chloride, solution of 20 per cent phosphotungstic acid, and hydrogen sulfide.

Procedure. Place 16.25 grams (weighed to within 0.03 gram) of the well-mixed feed in a small beaker and extract the fat with a 100-cc. portion of ethyl ether, allowing it to stand for a short time. When the material has settled out completely, decant the ether. Allow to stand in a warm place to evaporate remaining ether. Transfer the sample to a 300-cc. volumetric flask with 200 cc. of distilled water, and digest in a hot water bath with occasional shaking for a period of 30 minutes. Cool and fill

to volume with distilled water, then centrifugalize off the insoluble material.

Place 150 cc. of this solution in a 200-cc. flask. To this add 100 mg. of animal diastase, 75 mg. of invertase-melibiase scales, and 1.5 to 2 grams of yeast. After fermentation at a temperature of 24.4° to 26.67° C. (76° to 80° F.) for a period of 40 to 48 hours, make up to volume and centrifugalize to separate the yeast. Boil down 190 cc. of the liquid to about 25 or 30 cc. and wash into a 100-cc. volumetric flask by the aid of hot distilled water. To this add 10 cc. of saturated neutral lead acetate. Make up to volume with distilled water, and remove the precipitate by centrifugalizing. To 50 cc. of the resulting liquid in a 100-cc. volumetric flask add 2.5 cc. of a 5 per cent solution of mercuric chloride and allow to stand for a short time (20 to 30 minutes) with repeated shakings, after which add 5 cc. of a 20 per cent solution of phosphotungstic acid. Make up to volume with distilled water, and separate the precipitate by means of the centrifuge.

If the resulting solution has any suspended precipitate, filter through a dry filter paper before carrying further. Saturate the resulting liquid with hydrogen sulfide gas and filter. Next pipet 50 cc. of the clear, colorless solution into a 300-cc. Erlenmeyer flask, and boil until no hydrogen sulfide is given off. Then make up volume to 50 cc. and determine the lactose by the Munson & Walker method. Consistently better results are possible with the Jena fritted-glass filtering crucible I G 4 than with an asbestos mat in a Gooch crucible.

After thoroughly washing the precipitate, dissolve it with 5 cc. of 1 to 1 nitric acid, and determine the copper by the volumetric sodium thiosulfate method (*1*). The milligrams of lactose are interpolated from the Munson and Walker table (*1*).

Calculation

To obtain the number of grams of dry material used in the aliquot, Formula 1 is used:

$$\frac{150}{(300-8)} \times \frac{190}{200} \times \frac{50}{100} \times \frac{50}{(100-1)} \times 16.25 = 2.003 \text{ grams} \quad (1)$$

These figures are the dilutions which are made in the method and the (300 − 8) and (100 − 1) allow for a correction of 9 cc. for volumes of precipitates. As 2.003 grams are very nearly 2.000 grams and well within experimental error, 2.000 grams have been used in all further calculations.

To obtain the percentage of lactose in the feed, Formula 2 may be used:

$$\frac{(X-0.005)}{0.90 \times 2} \times 100 = \text{per cent of lactose in feed} \quad (2)$$

X = grams of lactose determined
0.005 = correction for blank
0.90 = lactose factor for fermentation loss
2 = weight of dry material in aliquot used as derived in Formula 1

When dry skim milk is the dairy product used in the feed mixture, it is possible to compute its percentage from the percentage of lactose present. On hundreds of samples of dry skim milk from all parts of the country, examined in this laboratory, the lactose content was found to be from 48 to 52 per cent. The average lactose content is approximately 50 per cent. The formula for calculating the amount of dry skim milk in feed is as follows:

$$\frac{\text{Per cent of lactose}}{.50} = \text{per cent of dry skim milk in feed}$$

0.50 = 50 per cent = per cent of lactose in dry skim milk

If dried buttermilk is the dairy product, then the lactose content of that material will have to be substituted in the above formula in place of the lactose content of dry skim milk. Dried buttermilk, especially when neutralizer is used, has a widely varying lactose content. Coe (*2*) has reported lactose contents of from 8 to 40 per cent. In recent years less variation has been noted and 36 per cent is suggested as a fair average value. The formula then becomes:

$$\frac{\text{Per cent of lactose}}{0.36} = \text{per cent of dried buttermilk in feed}$$

If dried whey is used as the dairy product in the feed mixture, the proper factor should be inserted in a similar formula. The lactose content of whey varies considerably, depending largely on the source of the whey.

There is no adequate or reliable method for determining the exact type of dairy product used in an unknown feed mixture. Only when the exact type of dairy product used is known may the lactose percentage be convertible into definite percentage of milk product.

Experimental

Preparation of Samples. In pursuing this work, it was necessary to make samples containing as many different meat, fish, and oil-meal products as possible, so that practically all combinations that are used in poultry mash feeds, in pig feeds, hog feed, concentrates, calf meals, etc., would be represented. These were hand-mixed in the laboratory.

Samples of mash and other feeds made by reputable manufacturers of open formula feeds were also used. Formulas were selected which contained no milk. These were checked for blank determinations and were also used after definite amounts of milk had been added. Various mineral mixtures were also added to feed mixtures in order to study their effect.

The following materials were used as feed ingredients of mixtures studied in the development of this method:

Ground Grains. Corn, wheat, oats, barley, milo, kafir, sunflower seed, buckwheat peas, hemp, common beans, millet, rye, soy beans.

Grain Products. Wheat bran, wheat middlings, wheat flour middlings, red dog flour, second clear flour, wheat germ meal, corn feed meal, hominy feed, corn gluten feed, corn gluten meal, barley feed, oat feed, clipped oat by-product, grain screenings, dried brewers' grains, dried corn distillers' grains, locust-bean meal, anise seed, and foenugreek.

Oil Meals. Corn-oil cake meal, linseed-oil meal, cottonseed-oil meal, soy bean–oil meal, sesame-oil meal, coconut-oil meal, and peanut meal.

Other Feed Ingredients. Alfalfa meal, alfalfa-leaf meal, dried beet pulp, cane (blackstrap) molasses, and charcoal.

Meat Products. Meat cracklings, meat scraps, tankage, blood meal, and blood flour.

Fish Products. White fish meal, menhaden fish meal, cod liver meal, sardine meal, and whale guano.

Vitamin D Oils. Cod liver oil, concentrated cod liver oil, and sardine oil.

Minerals. Ground oyster shell, ground limestone, steamed bone meal, spent bone black, rock phosphate, tri- and dicalcium phosphate, epsom salts, Glauber's salts, copperas, iron oxide, potassium iodide, common salt, sulfur, and wood ashes.

Protein Elimination. A number of protein precipitants were tried, both singly and in various combinations, before a suitable procedure was finally adopted. The final combination which was adopted as outlined in the foregoing procedure does not entail any close manipulation of conditions such as acidity, temperature, pH, etc., and results in a crystal clear, colorless solution. It is important to have the solution very slightly acid before the protein precipitations for it has been found that in alkaline solution some lactose may be lost in the procedure.

Sugar Elimination. It is necessary to eliminate all reducing sugars which interfere with the determination of the true percentage of lactose present in the feed mixture. Since the ingredients which are used in a complicated mixed feed contain widely varying types of sugars that are classified as reducing sugars and sugars nonfermentable by ordinary yeast, several enzymes must be used to bring about their fermentation from the original solution.

One of these sugars is raffinose, which is found in several of the ingredients of feed mixtures. On fermenting with ordinary yeast, it breaks down into levulose and melibiose, which is nonfermentable but is a reducing sugar. Melibiose was finally eliminated by the use of invertase-melibiase scales.

It was also found necessary to put in a small amount of animal diastase to speed up the starch hydrolysis, shorten the time of fermentation, and completely destroy reducing sugars other than lactose.

Fermentation. During the experimental work, it was found that fermentation time and temperature played a large part in the accuracy of the results. Many different temperatures and lengths of fermentation time were tried with varying results. This led to a 2-day fermentation in a cabinet, with controlled heat of 24.4° to 26.67° C. (76° to 80° F.) which produced accurate checks, and consequently was used in all following work. Higher temperature than this produced lactose loss.

Mold. During the study of fermentation times and temperatures, in a number of cases growth was found on the top of the fermented solutions, and under a microscope it was seen to consist of molds. In all instances where this substance was present the results were low. Whether these molds were carried through from the original feed material, or had been seeded along the line was not determined, but probably the contamination occurred in the laboratory. If samples show mold, they should be discarded and fresh samples started.

Lactose Determinations. It was necessary to try several different methods for the determination of lactose. The volumetric thiosulfate method (*1*) gave more satisfactory checks than gravimetric or direct determination of cuprous oxide. More satisfactory checks were also obtained by using a Jena fritted-glass filtering crucible, rather than an asbestos mat in a Gooch crucible, apparently because of a better retention of the copper oxide. The authors' findings on this were also substantiated by several workers in other laboratories. Colorimetric methods were not studied in this work.

Corrections

Feeds are made of moderately insoluble material. In many cases in this procedure, quite voluminous precipitates occur and therefore a correction in volumes should be made. It was found on measuring that the total volume of precipitates from the first extraction of the original feed was 7 cc. The next largest precipitate was that from the phosphotungstic acid precipitation which amounted to 1 cc. The remainder of the precipitates were calculated to be approximately 1 cc., making a total correction for precipitates of 9 cc. In the calculations for this method, this 9 cc. correction has been made in Formula 1.

The weight of the original sample of the dry material has been calculated so that the dry material represented in the aliquot taken for the lactose determination is 2 grams, thus simplifying further calculations. By using this method on over 100 samples of feeds containing no milk products, results were obtained representing approximately 0.25 per cent of lactose. It was found from these adjustments that 0.25 per cent should be subtracted from the results obtained, and this correction has been allowed for in the calculations under Formula 2, where 0.005 gram is subtracted from the grams of lactose determined in the feed.

On carrying the fermentation for two days at 24.4° to 26.67° C. (76° to 80° F.), there was some loss in the lactose. The cause of this loss was not determined but, in carrying a series of over 20 milk samples through the method, a loss of approximately 10 per cent of the total lactose was found. These results indicated that a 10 per cent lactose loss should be accounted for. This correction has been made in Formula 2, and is represented by the 0.90 in the formula.

After all the above corrections have been made, the results show this method can be depended upon to ±0.25 per cent of lactose.

Among the many ingredients which are used in the commercial feed mixes of today, only cane (blackstrap) molasses has given any difficulty in the above procedure. The trouble is due to the sugar "glutose" which is contained to the extent of 3 to 7 per cent in cane molasses, and is nonfermentable by ordinary yeast. At the present time, no enzyme or method of procedure has been found to eliminate such interference, but this is not important because very few feeds contain large amounts of molasses in combination with milk. It was found in the experiments that the presence of 5 per cent molasses indicated approximately 0.2 per cent of lactose, making it possible to make this correction on feeds containing molasses.

Results

Some of the results which have been obtained in this laboratory on known samples are listed in Table I. These results have been calculated into percentage of dry skim milk, as that was the dairy product used in making the samples. All the known samples were prepared outside the laboratory, and their dry skim-milk content was unknown to the laboratory until after the determination had been made and reported. Many other known samples were analyzed with equally satisfactory results.

Table I. Results on Known Samples

(All corrections made)

Type of Feed	Dry Skim Milk Added	Dry Skim Milk Determined
	%	%
Egg mash	None	None
Milk egg mash	4	3.97
		3.81
		4.29
Starter and broiler ration	8	8.23
		8.09
		8.09
Turkey starter	12.5	12.87
		13.34
		12.64
Hog supplement	5	4.64
Mixture (prepared in a state feed control laboratory)	None	0.29
	4.3	4.23
		4.63
	8.25	8.23
		8.40
Mash 6 per cent	6	6.12
		6.15
Hog supplement	8.9	9.05
Hog meal	None	None
	5.94	5.95
Egg mash	4.75	4.62
Laying mash	None	None
	7.45	7.50
	11.86	12.29
Growing mash	4.46	4.14

Discussion

This method is fairly long and entails a considerable amount of work and time. The authors believe, however, that it has been simplified as far as possible in keeping with the nature, variety, and number of feed ingredients used, or possibly used, in feed mixtures at present. No difficult or exceptionally closely controlled condition is necessary in this method except that of fermentation temperature.

The actual pH of the solution of any point of this procedure is of small consequence, except that at all times a solution alkaline to litmus must be avoided. Excessively high acidities which might interfere with fermentation should be avoided, but such conditions hardly come up in feed mixtures.

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Determination of Copper in Organic Matter

A Note on Ansbacher's Method

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An accurate method for the determination of small amounts of copper is of great importance to investigators in the field of nutritional anemia, and is essential to the correct interpretation of results obtained from investigations on the role of copper in hemoglobin regeneration. Unreliable methods for the determination of copper are doubtless partially responsible for the conflicting opinions which exist in this field of research.

For several years the Department of Home Economics has been trying out copper methods in an attempt to find one which would prove satisfactory in the analysis of food materials. Modifications of the xanthate (*10*), the Biazzo (*7*), and the carbamate method as described by Callan and Henderson (*3*) were all tried out, but the results obtained were not reliable. (A recent modification of the carbamate method has been reported, *8*, which the authors have not tried.) The only method which has thus far given consistent results is one in which chromotropic acid is used. This method was developed by Ansbacher (*2*), but has not as yet been adopted by many investigators in the United States. It is applicable to a wide variety of biological materials. The authors have used it successfully for the analyses of vegetables and sirups, and Ansbacher and collaborators for the analyses of fruits, vegetables, milk, eggs, oysters, meat, and other animal products (*1, 2, 4*). The chief difficulty in the use of this method is the determination of the end point when titrating with the chromotropic reagent. The authors have been able to overcome this difficulty, and in addition have developed certain details of technic which it seemed worth while to report.

Method

Destruction of Organic Matter. If the material to be analyzed contains sufficient copper so that a small sample (1 to 5 grams) may be used, it can be wet ashed. If a larger sample is required, dry ashing is preferable. With certain materials which are difficult to ash, such as sirups, a combination of wet and dry ashing was found to be most satisfactory.

For this method the weighed sample is placed in a silica or platinum dish and ashed in an electric muffle. The initial temperature should be below 100° C. The heat is rapidly increased until the temperature reaches 450° C. If a stream of air is drawn through the furnace, less time is required for ashing and a more complete ash is obtained. The time required is about 2.5 hours, varying with the nature of the material. The ash is washed into a 300-cc. Kjeldahl flask with copper-free distilled water; the dish is washed with 10 cc. of concentrated sulfuric acid, which is added to the ash. The latter is digested for 10 minutes, adding 1 cc. of 60 per cent perchloric acid if necessary to clear the solution, and transferred to a 300-cc. Erlenmeyer flask.

Precipitation of Copper and Solution of Copper Sulfide. The procedure is the same as that described by Ansbacher with the following modifications:

Instead of placing the crucible containing the copper sulfide in a glass triangle over a crystallizing dish, it is placed in a 50-cc. Erlenmeyer flask, the top of which has been cut off so that the crucible will fit into it to a depth of about 1.25 cm. (0.5 inch). A lip is also made in one side of the flask for pouring and rinsing out the copper nitrate and sulfate solution. The use of the Erlenmeyer flask decreases the danger from copper contamination, and loss of the sample due to the crucible tipping over.

To dissolve the copper sulfide and evaporate the copper nitrate and sulfate solution the Erlenmeyer flask is placed on an aluminum water bath which rests on an electric hot plate having aluminum top and sides. The hot plate is placed in a metal-free hood lined with asbestos sheet rock. Evaporation to dryness can usually be completed on the water bath, but it may be necessary to place the flask directly on the hot plate for a few minutes. It is also desirable, as Ansbacher suggests, to have a glass plate over the crucible and flask to exclude copper contamination.

Interfering Elements. The authors have encountered no difficulty with interfering elements in the foods analyzed. Ansbacher found that other metals which might occur in biological materials, including those of the second group, did not interfere with the method (*5*).

However, if an excess of sulfur is present the final solution is acid instead of neutral. When fuming nitric acid is used in wet ashing, a part of it may remain after digestion, and when hydrogen sulfide is passed through the solution considerable free sulfur is precipitated. This forms sulfuric acid in the subsequent treatment with fuming nitric acid, producing an acid residue on evaporation. When an unknown quantity of acid remains in the final solution, it is impossible to determine the quantity of ammonia to add without the use of an indicator. If the solution is too acid or too alkaline, low results are obtained. Sulfuric and perchloric acids alone are, therefore, used in wet ashing, although nitric acid may also be used if care is taken to remove all of it after the digestion is completed. This may be done by cooling the digest, adding 3 volumes of water, and concentrating by rapid boiling.

Preparation of Chromotropic Reagent. The sodium salt of the nitroso-chromotropic acid is made by dissolving 0.35 gram of chromotropic acid (Eastman Kodak Co. No. 1613) in 5 cc. of water and adding 0.21 gram of sodium carbonate, 0.5 cc. of 2 *N* sodium nitrite, and a slight excess of dilute acetic acid. Otherwise, the method described by Ansbacher for making up and standardizing the chromotropic reagent is followed.

Determination of Copper. When titrating with the chromotropic reagent, a colorimeter was first used to determine the end point, since the change in color from a purple to a brown tinge could be detected by this means when it could not be detected by the naked eye. When the eye becomes trained to observe the slight color change, it is not necessary to use the colorimeter.

In standardizing the chromotropic reagent as well as in the determination of copper in the unknown, the authors use a

series of four or more test tubes containing the same aliquot of standard or unknown. To obtain the best results, a 5-cc. aliquot should contain from 3 to 15γ (1γ = 0.001 mg.) of copper. Too dilute or too concentrated solutions give colors which make it difficult to determine the end point. A preliminary titration will show the approximate amount of copper in the unknown after the titer has been determined for the chromotropic reagent, which is added to the aliquots in gradations of 0.1 cc. At one end of the series the color in the test tubes should be distinctly purple, at the other end distinctly brown. The first aliquot which shows a brown tinge when examined in the colorimeter is taken as the end point.

Table I. Recovery of Added Copper

Sample	Copper in Sample	Copper Added	Total Copper Found	Added Copper Recovered	Copper Recovered
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	%
13 (sirup)	4.38	1.27	5.67	1.29	101.6
9 (sirup)	8.34	1.27	9.66	1.32	103.9
307 (peas)	73.30	2.30	75.40	2.10	91.3
308 (peas)	73.00	4.60	78.00	5.00	108.7
309 (peas)	71.50	11.50	82.50	11.00	95.6
310 (peas)	81.20	23.00	104.50	23.30	101.3
104 (sirup)	2.90	37.70	42.90	40.00	106.1
105 (sirup)	3.50	50.90	54.10	50.60	99.4

The authors were unable to distinguish differences in color where less than a drop of the chromotropic reagent was used. If the reagent was equivalent to 6.7γ of copper per cc., one drop or 0.05 cc. would be equivalent to 0.335γ of copper. Ansbacher found the reagent to be accurate to 0.5γ of copper.

Table I shows the recovery of copper added to sorghum sirup and peas.

Note. After this manuscript was submitted for publication, two papers of interest with regard to copper methods were published (*6*, *9*).

Conn and collaborators (*6*) make the following statement with regard to the four copper methods which they employed: "Summarizing experience with these four methods, the chromotropic acid method can be eliminated because of the difficulty in distinguishing the end point. The Biazzo method is not sufficiently sensitive. The possibility of interference due to turbidity makes the xanthate method undesirable. The carbamate method appears to be by far the most desirable, since it is the most sensitive, and the disturbing factor of turbidity is not encountered." The authors' results as well as those of Ansbacher (*1*, *2*, *4*, *5*) and Ohlson (*9*) have demonstrated that the chromotropic acid method is at least as sensitive as the carbamate method of Conn and collaborators, and apparently more reliable, judging by a comparison of the data on recovery of added copper for the two methods.

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Adsorption of Organic Liquids by Cellulose Products

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Attention has recently been called by Mease (*6*) to the fact that other liquids than water may be held tenaciously by fibrous materials. The same conclusion has been arrived at independently by Booth (*1*) and Wiertelak (*8*) in connection with standard analyses performed on cellulose and wood products. In case the samples analyzed contained but minute amounts of extractives, they were found to weigh more after extraction with an organic solvent, such as a benzene-alcohol mixture, and subsequent drying to constant weight than before the extraction, although the solvent undoubtedly contained some extracted substances.

This study was therefore undertaken in order to extend the scant information offered by Mease as well as to ascertain to what extent the adsorption of organic liquids may interfere with standard analyses of wood and cellulose products, as they are usually performed in technical laboratories.

Experimental

Adsorption experiments have been performed on the following cellulosic substances: commercial adsorbent cotton; Cross and Bevan cellulose prepared from white birch, probably *Betula papyrifera*, Marshall; commercial viscose rayon and commercial nitrate rayon, both supplied by the Rayon Works at Tomaszów, Poland; and commercial cuprammonium rayon, supplied by the Bemberg Aktien Gesellschaft at Barmen, Germany. The chemical composition of these cellulose products is described in detail in a recent paper by Wiertelak (*8*).

The liquids used for adsorption were: commercial 95 per cent ethyl alcohol; methyl alcohol Kahlbaum; *n*-butyl alcohol Kahlbaum, *gereinigt;* *n*-propyl alcohol, Merck; commercial diethyl ether; benzene, Merck or Kahlbaum, *purum;* commercial gasoline, boiling range 100° to 150° C.; pyridine, Polish Coke Association, *purissimum;* a benzene-alcohol mixture, 1 to 2; and a benzene-alcohol mixture, 2 to 1. The two benzene-alcohol mixtures were prepared from commercial 95 per cent ethyl alcohol and Merck or Kahlbaum benzene. All liquids were redistilled repeatedly before use.

Most of the above cellulose specimens were used in air-dry condition, their moisture content being shown by a separate determination to amount to from 7 to 10 per cent on the basis of the oven-dry sample. Approximately 1 gram of the air-dry sample, accurately weighed, was placed in an Erlenmeyer flask and kept in a thermostat at 25° C. for 15 minutes in contact with 25 cc. of the liquid to be tested. Then it was filtered through an alundum crucible, dried in air in an electrical drying oven at 105° C. to constant weight, and weighed. In one series a sample of cotton was oven-dried at first, and then treated with the adsorption liquid. The rest of the procedure was the same as above. The percentage increase in the oven-dry weight due to adsorption, calculated on the basis of the oven-dry weight of the fibers before treat-

ment represents the adsorption value. The results are recorded in Tables I and II.

As is evident from Table I, if cotton is dried to the oven-dry state before immersion in the liquid, it adsorbs a higher amount of alcohol than in the air-dry condition; similarly, regenerated celluloses and Cross and Bevan cellulose obtained from wood adsorb more alcohol than cotton. Evidently the adsorption of alcohol by various cellulose products is a function of their state of degradation. Since it is known (*4*, *5*) that prolonged heating of cellulose products at low temperature causes their chemical modification, it may well be that oven-dried cotton, being already slightly degraded, adsorbs a higher amount of alcohol.

Table I. Adsorption of 95 Per Cent Ethyl Alcohol by Cellulose Products

(Results are expressed in percentage of oven-dry material)

	Expt. I	Expt. II	Expt. III	Average
Cotton	1.59	1.64	1.57	1.60
Cotton, oven-dry	1.94	1.93	1.93	1.93
Cross and Bevan cellulose	1.83	2.12	1.98	1.98
Viscose rayon	2.13	2.10	..	2.12
Nitrate rayon	1.74	1.64	1.67	1.68
Cuprammonium rayon	2.15	2.14	2.11	2.13

Table II. Adsorption of Organic Liquids by Cotton and Nitrate Rayon

(Results are expressed in percentage of oven-dry material)

	Cotton				Nitrate Rayon			
	Expt. I	Expt. II	Expt. III	Av.	Expt. I	Expt. II	Expt. III	Av.
Methyl alcohol	0.80	0.80	..	0.80	0.94	0.96	0.85	0.92
Ethyl alcohol	1.59	1.64	1.57	1.60	1.74	1.64	1.67	1.68
Propyl alcohol	2.65	2.64	..	2.65	1.19	1.19	..	1.19
n-Butyl alcohol	1.42	1.84	1.89	1.72	0.60	0.44	..	0.52
Diethyl ether	0.06	0	0	0	0.33	0.33	..	0.33
Benzene	0.21	0.28	0.22	0.24	0.01	0.02[a]	..	0
Gasoline	0	0	0	0	0.15	0	..	0.07
Pyridine	..	..	..	..	0.56	0.56	0.49	0.54
Benzene–ethyl alcohol, 2 to 1	2.22	2.37	2.33	2.31	2.33	2.81	2.75	2.63
Benzene–ethyl alcohol, 1 to 2	1.23	1.26	1.29	1.26	3.23	3.42	2.98	3.21

[a] Loss in weight.

The alcohol adsorbed on both cotton and nitrate rayon may be removed by washing the samples with water. The samples, when dried carefully, return to their original oven-dry weight only if air-dry samples have been used in the adsorption experiments. When oven-dry cotton has been used a stronger washing, preferably with warm water, is needed. The same removal of alcohol from the cellulose samples can be attained by treating them with diethyl ether and drying. The samples assume their original oven-dry weight.

Attempts were made to isolate the adsorbed alcohol by treating 20 grams of cotton with alcohol, drying, and subsequently washing with 500 cc. of cold water. The washings were distilled and in the 250 cc. of collected distillate alcohol was determined by Rozman's titration method with standard permanganate (*7*).

In two determinations an almost quantitative yield was obtained.

	Gram	%
Alcohol adsorbed on 20 grams of cotton:		
By difference in weight	0.21	1.12
By titration with potassium permanganate	0.2032	..
	0.1995	..
Av.	0.2014	1.07

Extraction of Wood Samples with Benzene-Alcohol Mixture

The above results, especially those with benzene-alcohol mixtures, indicate that cellulose products adsorb a quantity of liquid, which even by prolonged heating cannot be removed from the samples. Since in standard analyses on wood and other cellulose products extraction with some organic solvent, especially with a benzene-alcohol mixture, is usually applied, it appeared of value to determine in what way the adsorption of the mixture by the fibers influences the final results.

Therefore extraction experiments with a benzene-alcohol mixture, 2 to 1, were performed on sawdust, which was at hand in the laboratory: loblolly pine sapwood, 40 to 60 mesh sample; white fir, heartwood, 60 to 80 mesh; eastern white pine, 40 to 60 mesh; and white birch, 60 to 80 mesh. The extraction was performed in a Soxhlet apparatus, and the extracted sawdust in the alundum crucible was weighed after drying, as prescribed in the standard methods compiled by Bray and Wiertelak (*2*, *3*). On the other hand, the extraction liquid in the Soxhlet flask was evaporated, and the amount of extractives determined by weighing. On the assumption that drying the extractives did not induce any chemical change, this represented the true value for the extractable matter. If the benzene-alcohol mixture was adsorbed in the sawdust analyzed, the value for the extractable matter, obtained by the difference in weight of the oven-dry sawdust before and after extraction, would be smaller than the above true value—viz., differing by the weight of the adsorbed benzene-alcohol mixture. The results, representing average values of at least four extractions, are compiled in Table III.

The results in Table III prove that the benzene-alcohol mixture is indeed adsorbed by the sawdust, since all true values for the extractive content of sawdust are higher than those obtained by weighing the sawdust before and after extraction. The difference is in some instances as high as 20 per cent.

Table III. Benzene-Alcohol, 2 to 1, Extractives in Sawdust

(Expressed in percentage of oven-dry weight of wood)

Species	True Value, by Weighing Extractives	Low Value, by Weighing Sawdust	Difference[a]
	%	%	%
Loblolly pine sap	5.02	4.97	1
White fir heart	2.69	2.18	19
Eastern white pine	12.45	11.43	8.2
White birch	2.40	1.99	17.1

[a] Based on the true value.

Summary

It is shown that various cellulose preparations adsorb alcohols, pyridine, and especially benzene-alcohol mixtures. The adsorbed liquid is not removed from the fibers even by prolonged heating at 105° C., but may be removed by washing with ether or water. Ether, benzene, and gasoline are not adsorbed. The adsorption causes a marked lowering of the value for the extractive content of sawdust, if that value is determined by weighing the sawdust.

Acknowledgment

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Determining the Correct Weight of Sample in Coal Sampling

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A mathematical treatment of the theory of coal sampling for float-and-sink determinations is developed and the results are shown to agree well with practical sampling tests. Methods are suggested for the actual use of the theory to determine sample sizes. The theory of sampling for ash analysis is sketched; this is a more complex problem and the theory cannot be applied without extensive tests, so that its use is limited to the large producers. The use of duplicate samples to determine sampling errors is illustrated. The gross error of sampling and analysis is frequently greater than the lot-to-lot variation in coal from the same source.

The first attempt to give a reasonable explanation of the quantitative errors in coal sampling for ash, and to determine suitable sample sizes, was made by Bailey (*1*). His samples were expected to give an accuracy such that 99.99 per cent of the results would fall within ±1 per cent of the actual ash. His tables were based upon the assumption that the coal being sampled would contain 5 per cent of ash as pieces of free slate, and that the largest pieces of slate would weigh two or more times the weight of the heaviest pieces of coal. Through these unfavorable assumptions Bailey was led to propose sample sizes running up to 3800 pounds when the largest pieces of slate were 2-inch, and 20 tons when they were 4-inch.

A recent and more successful attempt to apply empirically the theory of probability has been made by Grumell and Dunningham (*3*). These workers have taken account of the effect of varying percentages of ash and have arrived at sample sizes of a practical magnitude, which have been adopted by the British Standards Association. The concept of "average error" as a characteristic of a particular coal, as used in this work, is not clear in detail, but it seems to involve a larger variability from car to car than is found in most American coals.

The only attempt which has previously been made to calculate theoretically what the sampling errors will be, without the help of empirical sampling tests, is due to Findlay (*2*). This work is entirely incorrect, however, and must be disregarded.

The present work is concerned largely with float-and-sink sampling, which is simpler both theoretically and practically. An indication is given of how the methods used could be applied to sampling for ash, sulfur, B. t. u., etc., but it is not possible to put the results into very useful form.

Theory of Float-and-Sink Sampling

It will be helpful to consider first the simplified case of a coal in which all pieces have the same weight. Let f be the fraction of the pieces which will sink at some specified gravity, and $(1 - f)$ the fraction which will float. If a random sample of n pieces is taken it may contain any number of pieces of sink from 0 to n. The chance that it will contain just r pieces of sink is well known to be

$$\frac{n!}{r!\,(n-r)!} f^r (1-f)^{n-r}$$

The derivation of this formula can be found in any treatise on probability. It may be worth while to give a table calculated for the values $f = 0.06$, $n = 100$. (See Table I.) Findlay gives for $r = 10$ the wholly incorrect probability 0.0001.

Such a table gives complete information, but it is too cumbersome for ordinary use. Fortunately, it is usually sufficient to give only the standard deviation, which is the square root of the average of the squares of the individual deviations from the average. It can be shown that if a large number of samples of n pieces each are taken, the average number of pieces of sink per sample will approach nf, and the standard deviation $\sqrt{nf(1-f)}$. The standard deviation in the fractional weight of sink, which is of more direct interest, is of course $\sqrt{f(1-f)/n}$. In practical application, f will almost always be less than 0.1, and it will then make no significant error to drop the factor $(1 - f)$ and write the standard deviation as $\sqrt{f/n}$.

From Table I it is clear that the distribution of errors is quite unsymmetrical, the small errors being predominantly negative and the large ones predominantly positive. As nf becomes larger, the distribution becomes more and more symmetrical, and in the limit goes over to the Gaussian distribution, the so-called Normal Law of Errors. When the normal law is obeyed the error will exceed 0.6745 times the standard deviation just half the time; once in 100 times it will exceed 2.57 times the standard deviation; and once in 10,000 times it will exceed 3.89 times the standard deviation. For the example given, with $nf = 6$, 0.6745 times the standard deviation is 1.65 pieces, and an error of 2 or more pieces occurs 53 times in 100; 2.57 times the standard deviation is 6.3 pieces, and an error of 7 or more pieces occurs once in 144 times; 3.89 times the standard deviation is 9.5 pieces, and an error of 10 or more pieces occurs once in 3300 times. When nf is greater than 10, the normal law is accurate enough for all practical purposes.

Table I. Calculated Probability

r	Probability	r	Probability
0	0.00206	10	0.0400
1	0.0131	11	0.0209
2	0.0415	12	0.0100
3	0.0865	13	0.00431
4	0.134	14	0.00171
5	0.164	15	0.000625
6	0.166	16	0.000212
7	0.142	17	0.000069
8	0.105	18	0.000020
9	0.0688	19	0.000007

For application to actual coal-sampling problems, it is necessary to generalize this by permitting the pieces to have different weights. Suppose that the coal being sampled contains per pound n_1 pieces of sink of weight w_1, n_2 pieces of weight w_2, . . . , the total fractional weight of sink being $f = n_1w_1 + n_2w_2 + \ldots$, which will again be supposed to be fairly small. Then a sample of weight W will contain on the average Wn_1 pieces of sink of weight w_1; the standard deviation in number will be $\sqrt{Wn_1}$ and in weight will be $\sqrt{Wn_1}\,w_1$. A similar expression holds for each set of sink pieces; the stand-

ard deviation in the total weight of sink is given by the square root of the sum of the square of the single standard deviations (this is a poor approximation when f is too large) and hence is $\sqrt{W}\sqrt{n_1w_1^2 + n_2w_2^2 + \ldots\ldots}$ The standard deviation in the fractional weight of sink is then

$$\sqrt{1/W}\sqrt{n_1w_1^2 + n_2w_2^2 \ldots\ldots}$$

It is convenient to invent an effective piece weight W^*, defined by

$$W^* = \frac{n_1w_1^2 + n_2w_2^2 + \ldots}{n_1w_1 + n_2w_2 + \ldots} \qquad (1)$$

In terms of this effective weight, the standard deviation in the fractional weight of sink material in a sample of weight W is given by

$$\sigma = \sqrt{fW^*/W} \qquad (2)$$

The coal has thus the same sampling behavior it would have if all the sink were replaced by the same total weight of sink each piece of which had the weight W^*. Thus, if W^* is known it is possible to predict just what errors may be expected for any given weight of sample. When the weights of each individual piece of sink from a large enough sample

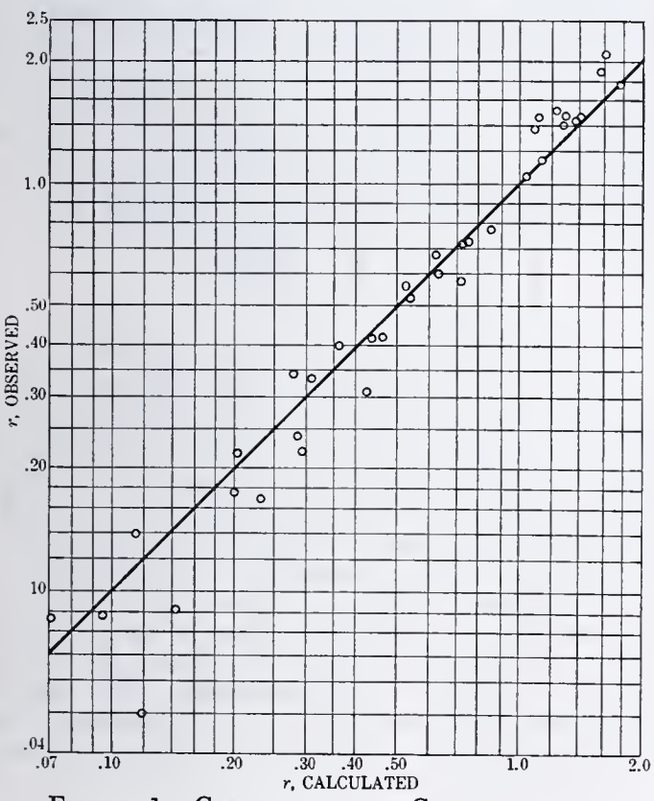

FIGURE 1. COMPARISONS OF CALCULATED AND OBSERVED VALUES

have been determined, W^* may be calculated as above by dividing the sum of the squares of the weights by the sum of the weights. For practical cases it will often be necessary, and always sufficient, to use a screen analysis, giving the total weight of sink in various size ranges. Then, if f_1 is the fractional weight of the total sink material which is in the size range with estimated mean weight w_1, and likewise for the other ranges

$$W^* = f_1w_1 + f_2w_2 + \ldots \qquad (3)$$

Some calculations based on hypothetical coal-sink mixtures are shown in Table II. It is clear that in such a case the errors in sampling are due almost entirely to the relatively few heavy pieces of sink. The effective piece weight will always be less than the maximum and more than the average weight of the pieces of sink.

TABLE II. CALCULATED SAMPLING ERRORS

SINK PER 1000 POUNDS		W^*	STANDARD DEVIATION 100-POUND SAMPLE
	%	Lb.	%
5 1-pound pieces	= 0.5	1.000	0.707
+ 10 8-ounce pieces	= 1.0	0.750	0.866
+ 20 4-ounce pieces	= 1.5	0.583	0.936
+ 40 2-ounce pieces	= 2.0	0.469	0.968
+ 80 1-ounce pieces	= 2.5	0.387	0.984

The practical validity of such calculations has been well established by a number of tests for coals of varying characteristics. It will be sufficient to give a single example in detail.

Twenty samples of prepared egg coal were collected over an operating period of about 8 hours. After removal of undersize through a 1-inch screen the samples weighed 97 to 103.5 pounds. All of each sample was separated at gravities of 1.45 and 1.60. Each batch of 1.60 sink and of 1.45 sink–1.60 float was divided by a screen analysis into plus 3-inch, 3 × 2-inch, 2 × 1-inch, and 1 × 0-inch, and the number and total weight of material in each division were determined. It will not make an important error to assume that the divisions which contained more than a single piece contained pieces each of which had exactly the average weight, since such grouping does not occur for the heaviest pieces of major importance. The distributions actually found for the 20 batches were as follows:

No. of Pieces	Weight	No. of Pieces	Weight	No. of Pieces	Weight	No. of Pieces	Weight
	Oz.		Oz.		Oz.		Oz.
			1.60 SINK				
1	24.5	1	8	3	3.2	6	2.0
1	15.5	1	7	12	3.0	2	1.8
1	14	1	6	4	2.9	7	1.6
1	12.5	5	5.6	3	2.7	6	1.5
1	12	4	5.4	5	2.6	12	1.3
1	10	2	4	1	2.5	13	0.85
			1.45 SINK–1.60 FLOAT				
2	10.5	1	5	1	3	9	1.5
1	9.5	3	4.33	2	2.75	5	1.4
1	9	10	4.1	3	2.2	9	1.33
1	7	6	4	4	2.0	9	1.11
2	5.25	1	3.5	5	1.6	12	0.92

From these figures it is easy to calculate that the effective piece weight for the 1.60 sink is 7.15 ounces or 0.447 pound; for the 1.45 sink–1.60 float, 4.33 ounces or 0.271 pound; and for the entire 1.45 sink, 5.96 ounces or 0.372 pound. An estimate of the precision of these figures may be obtained by noting that if the heaviest piece of 1.60 sink had been absent the effective weight would have been 0.354 pound, while if there had been two pieces of this weight the effective weight would have been 0.526 pound.

The weight percentages of material in the various fractions for each of the 20 samples were as follows:

1.60 Sink	1.45–1.60 Sink	1.45 Sink	1.60 Sink	1.45–1.60 Sink	1.45 Sink
2.32	1.64	3.96	0.85	1.17	2.02
2.11	0.79	2.90	0.80	0.67	1.47
1.73	0.50	2.23	0.76	0.51	1.27
1.72	0.28	2.00	0.59	0.66	1.25
1.41	0.85	2.26	0.58	0.19	0.77
1.26	1.26	2.52	0.54	0.73	1.27
1.04	0.68	1.72	0.51	1.02	1.53
1.02	0.77	1.79	0.12	0.37	0.49
0.92	1.05	1.97	0.09	0.41	0.50
0.87	0.38	1.25	0.03	0.47	0.50

In this table the 20 samples have been arranged in order of decreasing 1.60 sink, and the 1.45–1.60 and 1.45 sink percentages for the same sample are given on the same line. From these results we can calculate at once the average sink percentage and standard deviation in each classification, while from the average percentage and the previously obtained effective piece weights we calculate the expected standard deviation. The results are:

CLASSIFICATION	PERCENTAGE	σ, ACTUAL	σ, EXPECTED
1.60 sink	0.963	0.621	0.656
1.45–1.60 sink	0.720	0.359	0.443
1.45 sink	1.683	0.841	0.793

The agreement is quite good; the relatively larger actual standard deviation for the composite 1.45 sink indicates that the fundamental assumption back of these calculations—namely, that the sink material is distributed throughout the coal individually and collectively at random—is not quite fulfilled. In simpler language, this means that the coal is not perfectly mixed. It is nevertheless sufficiently well mixed so that these methods of calculation have real practical value. Further evidence on the

extent of mixing is found in the weights of sink in the separate samples. The 10 samples highest in 1.60 sink averaged 1.44 per cent, the other 10, 0.487 per cent; for the same grouping, the 1.45–1.60 material gave 0.82 and 0.62 per cent, respectively. A calculation shows that the standard deviation of the difference between these last two averages is 0.15 per cent; the difference is thus twice its own probable error and is therefore likely to be real.

A large number of similar tests have been made on various coals covering a range of probable error from 0.05 to 2.0. These tests permit 36 comparisons of calculated and observed values, based on a total of 2456 float-and-sink determinations on samples of from 22 to 107 pounds. These comparisons are shown in Figure 1, where the distance between the points and the solid line shows the extent of agreement; in only one case is there serious disagreement, and here the calculated error exceeds that observed. It is evidently possible to use Formulas 2 and 3 to determine a suitable size of sample.

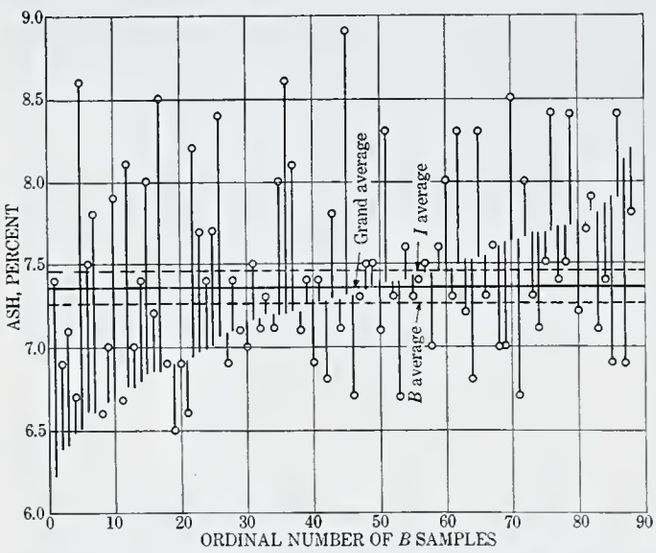

Figure 2. Typical Result of Sampling for Analysis

The way these formulas will be used will naturally vary somewhat with the other conditions of the test. Whenever coal of essentially constant character is being tested repeatedly, it will be worth while occasionally to make an actual screen analysis. Suppose it is known from such analyses that the effective piece weight is 0.37 pound, and the expected percentage of 1.45 sink is 1.7; then if it is desired to take a sample large enough to assure an error of less than 0.25 per cent 99 times in 100, we have

$$\sqrt{0.017 \times 0.37/W} = 0.0025/2.57$$

from which $W = 6600$ pounds. It will very rarely, if ever, seem feasible to take so large a sample, and usually a lower standard of accuracy, say 1 per cent 99 times in 100, from a sample of 410 pounds, will have to be accepted. There are some cleaning plants, however, which produce coals with such low values of p and W^* that the standard of 0.25 per cent 99 times in 100 is easily attained for tests at 1.60 specific gravity or higher.

It saves calculation to rewrite Formula 2 in the form

$$W = 660\ pW^*/a^2 \qquad (4)$$

where p is the percentage of sink and a is the per cent error allowed once in 100 times. Here and throughout the paper per cent error is based on the total coal, not on the quantity being measured. This formula is so simple to use that there is no need to refer to a table. It is interesting, however, to see in a general way what weights are required under various conditions, and Table III is given for that purpose.

Table III. Sample Weights for Float-and-Sink Determinations

pW^* \ a	0.25	0.50	0.75	1.0	1.5	2.0
0.25	264	66	..	..	...	...
0.5	528	132	54	..	...	...
0.10	1056	264	117	66	...	...
0.25	2640	660	268	165	73	...
0.50	..	1320	537	330	147	82
1.0	..	2640	1173	660	293	165
1.5	..	..	1610	990	440	247
2.0	..	..	2147	1320	587	330
2.5	..	..	..	1650	733	412

It should be possible to estimate p and W^* by inspection before sampling. After the float-and-sink separation has been made, the value of p will be at least approximately known, and a much better estimate of W^* can be made. This second value of pW^* provides a valuable control on the process.

Values for W^* ordinarily will fall in the following ranges:

2 × 3 inch, round	$W^* = 0.08$ to 0.30 pound
2 × 4 inch, round	$W^* = 0.20$ to 0.60 pound
Larger sizes	$W^* = 0.20$ to 2.0 pounds

When no other information is available, the upper limit of the appropriate range may be assumed, together with a value $p = 2$ (2 per cent sink).

It is suggested that three basic standards of accuracy be set up. Standard C, for ordinary commercial analysis, has a standard deviation of 0.39 per cent and a once-in-100 error of 1.0 per cent. Standard A, for research purposes, has a standard deviation of 0.19 per cent and a once-in-100 error of 0.50 per cent. Standard B is intermediate, with a standard deviation of 0.28 per cent and a once-in-100 error of 0.71 per cent. The weights necessary to give these results are

A	$W = 2640\ pW^*$
B	$W = 1320\ pW^*$
C	$W = 660\ pW^*$

Formal Theory of Sampling for Analysis

The problem of sampling for analysis (ash, sulfur, B. t. u., etc.) presents two new features not found in float-and-sink sampling; these are the process of reduction and the change from qualitative to quantitative differences. For a fixed density of separation, each piece fell into one of two sharp classes, Float or Sink, and nothing else had to be considered. In sampling for analysis, however, we must take account of the fact that a piece may have any ash value from nearly zero up to over 100 per cent, and wide ranges for other properties as well. When sufficiently detailed figures are available with regard to the piece-by-piece composition of the coal, the sampling error can be calculated. Thus, if per pound of coal there are n_i pieces with weight w_i and ash per cent p_i, the coal will have an ash per cent

$$P = \Sigma n_i p_i w_i$$

and the standard deviation in ash for a sample of weight W will be

$$\sigma = \sqrt{1/W}\ \sqrt{\Sigma n_i (p_i - P)^2 w_i^2}$$

In large, clean coal almost all the really high-ash pieces have relatively low weights; some data are available on the product of highly efficient cleaning plants, which show that the pieces with over 25 per cent ash have a negligible effect, and the sampling error is due almost entirely to the variation in ash of the coal itself. In small, dirty coal the situation is reversed, and the sampling error is due almost entirely to the refuse. In no case are enough data available to make a prediction of the sampling error from the composition of the coal. It would require a great deal of work to obtain enough data, and probably in most cases this would not be justified. Large

producers, however, might find it worth while to put their sampling on a sound basis in this way.

Under some conditions it is possible to estimate from sampling records what the actual over-all error in sampling, reduction, and analysis has been. Thus, suppose that we have two or more check samplings on successive lots of coal from the same plant; if the actual variability of the coal corresponds to a standard deviation δ and the sampling errors of the two series correspond to standard deviations ϵ_1 and ϵ_2, respectively, the ash values in the separate series should show standard deviations $\sqrt{\delta^2 + \epsilon_1^2}$ and $\sqrt{\delta^2 + \epsilon_2^2}$, and the differences between the two samples on the same lot should show a standard deviation $\sqrt{\epsilon_1^2 + \epsilon_2^2}$. These three relations permit the determination of δ, ϵ_1, and ϵ_2. This has been done in a number of cases. Figure 2 shows a typical result.

In this case 88 cargoes of 1000 to 1400 tons of nut and slack through a 2.125-inch bar screen were sampled by producer *B* and by consumer *I*. The *B* samples were taken by increments of 1.5 pounds as the nut and slack coal flowed into the car, an increment being taken every time a mine car (1-ton capacity) was dumped. The gross samples, which always weighed more than 1500 pounds, were crushed and reduced by hand; a 3-pound can was sent to the laboratory. The consumer took a 500-pound gross sample by automatic machinery; this was crushed mechanically, reduced, crushed to 10-mesh, reduced again, and crushed again to 60-mesh to give the *I* samples. Standard methods of analysis were used in both cases. In Figure 2 the 88 cargoes have been numbered in the order of increasing ash as found by *B*, and the results of both *B* and *I* then plotted against the cargo number. The two corresponding analyses appear at the two ends of a line, that made by *I* being marked with a circle. It is obvious from a glance at Figure 2 that there is almost no connection between the results found by *B* and *I* for identical lots of coal. Calculation shows that the *B* samples have a standard deviation of 0.37 per cent and the *I* samples of 0.55 per cent, while the true ash in the cargoes has a standard deviation of only 0.18 per cent.

Reference to tables of the probability integral then shows that while the *I* samples are in error by at least 1 per cent seven times in 100 and the *B* samples seven times in 1000, a cargo of coal will differ by 1 per cent from its average value less often than once in 10 million times. This last result is misleading, as the distribution is certainly not Gaussian at the extreme ends, and many contingencies which were absent for 88 consecutive cargoes might occur once in several thousand times with a resultant large effect on the ash. Nevertheless, the chances are excellent that any particular abnormal ash value does represent a sampling error.

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Viscosity Data for Commercial Rosin and Abietic Acid

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The viscosities of some amorphous samples of commercial wood rosin and abietic acid have been measured in absolute units within the temperature range 28° to 135° C. These measurements, while they were made primarily as a part of an extensive investigation of liquids that form glasses or amorphous solids on cooling, possess considerable technical interest in themselves; hence, the results will be briefly summarized here. In a sense they serve to supplement the earlier study by Peterson and Pragoff (*3*) on the viscosity of rosins, which covered the temperature range 125° to 200° C.

The samples of commercial wood rosin and abietic acid investigated were kindly supplied by the Hercules Powder Company. The rosin was of two grades—FF and I. The former was a dark brown material, which showed no tendency to crystallize. Analyses in the authors' laboratory yielded about 155 for its acid number. Rosin I was a purified, reddish amber material, which frequently crystallized when kept at moderately elevated temperatures for a day or more. Its acid number was 161. The commercial abietic acid was light yellow in color and had an acid number of 170.5.

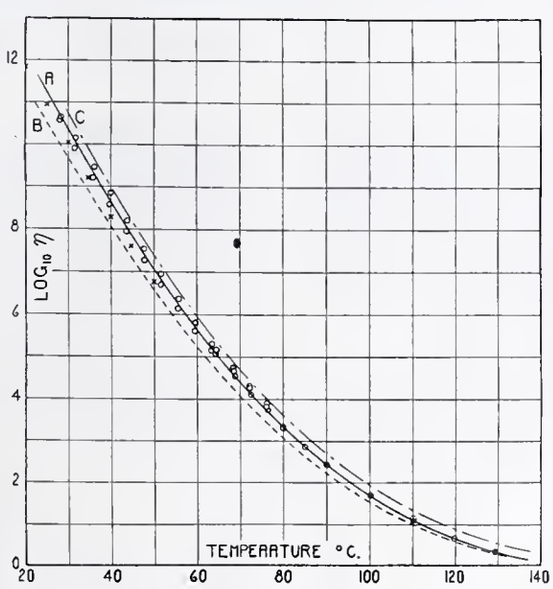

Figure 1. Logarithm of Viscosity Plotted against Temperature

A, commercial abietic acid; *B*, wood rosin I; *C*, wood rosin FF. In the case of abietic acid the circles represent individual values obtained in the present study, the heavy dots represent two or more values which practically coincide, and the crosses show the results of Bingham and Stephens.

The viscosity measurements above 80° C. were made by the falling-sphere method. For the use of this method the densities of the three substances were required and accordingly these were measured at 100°, 130°, and 160° C. with a Pyrex specific gravity bottle. The resulting values conformed closely to the linear equations:

Rosin FF, $d = 1.094 - 0.0006\,t$
Rosin I, $d = 1.075 - 0.0006\,t$
Abietic acid, $d = 1.077 - 0.0006\,t$

where t refers to the Centigrade temperature. The viscosity measurements below 80° were made with a concentric cylinder viscometer. Full details concerning the apparatus and procedure with each method have been given by Parks, Barton, Spaght, and Richardson (*2*) in their work on undercooled liquid glucose. Temperature measurements, which generally represent one of the limiting factors in accurate viscosity

determinations, were made with thermometers calibrated by the U. S. Bureau of Standards and readable to ±0.02°.

In the course of the investigation forty-eight individual viscosity values were obtained with seven different samples of the abietic acid, forty-eight viscosity values with six separate rosin I samples, and thirty-one viscosity values with four rosin FF samples. In general, a series of values obtained with any one sample was found to lie very consistently on a smooth curve and to be highly reproducible, but apparently the various series with different samples of the two rosins and abietic acid could differ appreciably. This behavior is, perhaps, not surprising in view of the fact that the materials were commercial products and that viscosity is a property of matter which is often extremely sensitive to small differences in the composition and even in the preparation (thermal history) of the samples.

Figure 1, in which the common logarithm of the viscosity (in poises) has been plotted against the Centigrade temperature, shows all the viscosity results in the case of abietic acid. The smooth curve *A* appears to be fairly representative of these data, indicated by the circles and dots, which have been obtained in the present study. The crosses, lying somewhat below this curve, are the values for abietic acid recently published by Bingham and Stephens (*1*) as representative of the results found with their alternating stress method. In all cases the authors' results indicated true viscosity and not plasticity; and this was also the conclusion of Bingham and Stephens, who measured a viscosity as large as 7.2×10^{11} poises at 20° C.

Curves *B* and *C* serve to show how results for rosin I and rosin FF compare with those for the abietic acid. To avoid confusion in the figure the individual points for these data have been omitted. It is interesting that the darker, or cruder, rosin has an appreciably higher viscosity than the commercial abietic acid, while rosin I is consistently lower within the temperature range of this study. At the upper temperatures the authors' rosin curves overlap to some extent the viscosity determinations published by Peterson and Pragoff (*3*) and in this region the two investigations are in fair agreement. Thus for rosin I, Peterson and Pragoff found a viscosity value of 2.83 poises at 125° C., while curve *B* in the authors' study corresponds to 2.5 poises. In the case of rosin FF the earlier investigators found viscosities of 5.95 poises at 120° C. and 2.56 poises at 130° C.; and the present study yields 7.4 and 3.3 poises, respectively, at these two temperatures.

Table I. Viscosity Data for Wood Rosin and Abietic Acid

Temp. °C.	Rosin FF $\log_{10}\eta$	Rosin I $\log_{10}\eta$	Abietic Acid $\log_{10}\eta$
28	...	10.06	10.68
30	10.73	9.73	10.35
40	9.00	8.11	8.71
50	7.38	6.60	7.07
60	5.96	5.23	5.68
70	4.69	4.04	4.40
80	3.62	3.06	3.33
90	2.70	2.23	2.43
100	1.93	1.54	1.78
110	1.34	0.98	1.10
120	0.87	0.57	0.65
130	0.52	0.27	0.31

In Table I are given a series of "best values" for viscosity results with these three materials, obtained by reading off the $\log_{10}\eta$ values corresponding to even temperatures in an enlargement of Figure 1. For convenience in tabulation the data have been kept in the form of the common logarithm of the viscosity (in poises).

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A Rapid Method of Preparing Biological Materials for Phosphorus Determinations

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Difficulty has been encountered in preparing cattle and sheep urine for total phosphorus determinations. The low phosphorus content requires the digestion of large quantities of urine and the removal of the organic matter requires vigorous oxidation. In digesting with nitric and hydrochloric acid, it is practically impossible to obtain a clear solution. Sulfuric-nitric acid digestion with further addition of nitric acid or sodium nitrate requires 2 hours' digestion or more to clarify urine samples. The same method of digesting feeds and feces requires 1 to 2 hours.

The use of perchloric acid in combination with nitric and sulfuric acids or with sulfuric acid alone has been found to accelerate the clarification appreciably through rapid, vigorous oxidation. Twenty-five cubic centimeters of cattle urine are thus digested in 15 minutes and 2 grams of feed require about the same time. Phosphorus determinations on perchloric acid–digested samples have been found to be accurate and to compare well with determinations by official methods (*1*).

Very good recovery of added phosphorus has been made. Table I shows the accuracy with which phosphorus may be recovered from standard solutions gravimetrically, volumetrically, or colorimetrically, after perchloric acid digestion. Standard solutions of potassium phosphate were placed in Kjeldahl flasks and filter paper was added to supply organic matter. The organic matter was removed by oxidation with sulfuric, nitric, and perchloric acids, as in determinations of phosphorus on biological materials.

Table I. Recovery of Phosphorus after Perchloric Acid Digestion of Standard Solutions

(Phosphorus added as K_2HPO_4)

Gravimetric Method		Volumetric Method		Colorimetric Method	
Phosphorus added	Recovered after $HClO_4$ digestion	Phosphorus added	Recovered after $HClO_4$ digestion	Phosphorus added	Recovered after $HClO_4$ digestion
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
0.0060	0.0060	0.0017	0.0018	0.0057	0.0057
	0.0058		0.0019		0.0057
	0.0058		0.0017		0.0057
	0.0058		0.0019		0.0057
	0.0058		0.0018		0.0057
	0.0060		0.0018		0.0057

Table II. Phosphorus in Urine Samples by Colorimetric Method

(25-cc. duplicate samples of urine digested by each method)

Sulfuric-Perchloric Acid Digestion				Sulfuric-Nitric Acid Digestion				Difference between Methods
A[a]	B[a]	Difference	Av.	A	B	Difference	Av.	
%	%	%	%	%	%	%	%	%
0.0010	0.0009	0.0001	0.0009	0.0009	0.0009	0.0000	0.0009	0.0000
0.0009	0.0009	0.0000	0.0009	0.0009	0.0009	0.0000	0.0009	0.0000
0.0011	0.0011	0.0000	0.0011	0.0011	0.0012	0.0001	0.0011	0.0000
0.0022	0.0021	0.0001	0.0021	0.0022	0.0022	0.0000	0.0022	0.0001
0.0064	0.0063	0.0001	0.0063	0.0063	0.0064	0.0001	0.0063	0.0000
0.0125	0.0125	0.0000	0.0125	0.0125	0.0125	0.0000	0.0125	0.0000

[a] A and B are duplicates of the original sample treated in the same manner.

Table I shows good recovery of phosphorus in all cases. Satisfactory results were also obtained by comparing phosphorus found in biological materials after rapid perchloric acid digestion with that found after more tedious methods.

Digestion of Urine Samples

Twenty-five or 50 cc. of urine were pipetted into a 500-cc. Kjeldahl flask and 5 to 10 cc. of concentrated sulfuric acid were added. The flask was heated until copious white fumes were no longer evolved. One cubic centimeter of 70 per cent perchloric acid was added to the hot solution and the boiling continued. If the solution did not become water-clear in about 5 minutes, another 0.5 cc. of perchloric acid was added. The solution was boiled for a short time after becoming clear, cooled slightly, and 50 cc. of water were added cautiously. This was transferred to a volumetric flask, cooled, and made up to volume. The phosphorus was determined either volumetrically or colorimetrically.

A very offensive odor accompanied sulfuric acid digestion of urine up to the time the perchloric acid was added. When ventilation was poor, it was therefore found advantageous to add 10 to 15 cc. of concentrated nitric acid to the urine at the time sulfuric acid was added. The digestion was then completed with perchloric acid as before. The complete digestion required 15 to 25 minutes.

The results obtained by the rapid sulfuric-perchloric acid digestion and by the slower nitric-sulfuric acid digestion of aliquots of the same sample are given in Table II. Good checks were obtained by 0.0001 per cent, showing that the rapid method with perchloric acid is at least as accurate as the slower method.

Digestion of Feeds, Feces, and Fertilizers

Feeds, feces, and fertilizers have been digested for phosphorus determinations by heating 15 minutes with sulfuric, nitric, and perchloric acid. In many cases the use of nitric acid is unnecessary.

From 1- to 4-gram samples were placed in 500-cc. Kjeldahl flasks. Fifteen cubic centimeters of sulfuric acid were added, then 15 or 20 cc. of nitric acid. The flask was swirled to facilitate mixing, and heated gently under a small flame until danger of frothing had passed. The boiling was then continued with a full flame until copious white fumes were no longer evolved. One cubic centimeter of 70 per cent perchloric acid was added and the boiling continued. If the solution did not clear up in 5 minutes, another 0.5 cc. of perchloric acid was added. When the material oxidized with difficulty, it was sometimes found expedient to add a second portion of nitric acid at the time copious white fumes were evolved, and then to heat again to white fumes before adding the perchloric acid. It has rarely been necessary to add a second portion of nitric acid. The analysis was completed gravimetrically or volumetrically, with equally good results.

The author has used this digestion successfully in the analysis of several hundred samples for phosphorus during the past three years. Before applying the method to different types of material, samples were prepared by perchloric acid digestion in duplicate, and at the same time samples of the same material were digested by accepted procedures (*1*). The results are tabulated in Tables II, III, IV, and V. Data obtained from these comparisons are presented without choice or repetition, so that a complete picture of the comparison may be obtained. For both volumetric and gravimetric determinations official methods (*1*) were used after digestion was completed. The colorimetric method used was that of Zinzadze (*3*), modified to use Zinzadze (*2*) molybdenum blue reagent.

Table III. Phosphorus in Poultry Feeds by Volumetric Method

Digestion with $HClO_4$, HNO_3, and H_2SO_4				Digestion with $NaNO_3$, HNO_3, and H_2SO_4				Difference between Methods
A	B	Difference	Av.	A	B	Difference	Av.	
%	%	%	%	%	%	%	%	%
0.98	0.96	0.02	0.97	0.92	0.92	0.00	0.92	−0.05
0.97	0.83	0.14	0.90	0.97	0.95	0.02	0.96	+0.06
0.91	0.92	0.01	0.92	0.92	0.87	0.05	0.90	−0.02
1.07	1.03	0.04	1.05	1.06	1.11	0.05	1.09	+0.04
1.16	1.18	0.02	1.17	1.12	1.12	0.00	1.12	−0.05
0.55	0.54	0.01	0.55	0.52	0.50	0.02	0.51	−0.04
	Av.	0.04			Av.	0.02	Av.	0.04

Table IV. Phosphorus in Pasture Grass by Volumetric Method

Digested with $HClO_4$, HNO_3, and H_2SO_4				Ashed				Difference between Methods
A	B	Difference	Av.	A	B	Difference	Av.	
%	%	%	%	%	%	%	%	%
0.63	0.65	0.02	0.64	0.66	0.67	0.01	0.67	+0.03
0.61	0.63	0.02	0.62	0.67	0.64	0.03	0.66	+0.04
0.65	0.67	0.02	0.66	0.63	0.60	0.03	0.62	−0.04
0.65	0.66	0.01	0.66	0.58	0.66	0.08	0.62	−0.04
0.43	0.44	0.01	0.44	0.45	0.45	0.00	0.45	+0.01
0.45	0.45	0.00	0.45	0.45	0.43	0.02	0.44	−0.01
0.42	0.44	0.02	0.43	0.46	0.44	0.02	0.45	+0.02
0.66	0.66	0.00	0.66	0.60	0.60	0.00	0.60	−0.06
0.41	0.41	0.00	0.41	0.44	0.43	0.01	0.44	+0.03
0.42	0.41	0.01	0.42	0.45	0.45	0.00	0.45	+0.03
0.41	0.42	0.01	0.42	0.46	0.46	0.00	0.46	+0.04
0.46	0.48	0.02	0.47	0.47	0.46	0.01	0.47	0.00
	Av.	0.01			Av.	0.02	Av.	0.03

Table V. Phosphorus in Fertilizers by Gravimetric Method

Digested with $HClO_4$, HNO_3, and H_2SO_4				Digested with $NaNO_3$, HNO_3, and H_2SO_4				Difference between Methods
A	B	Difference	Av.	A	B	Difference	Av.	
%	%	%	%	%	%	%	%	%
4.29	4.26	0.03	4.28	4.34	4.24	0.10	4.29	+0.01
4.28	4.27	0.01	4.28	4.27	4.32	0.05	4.30	+0.02
2.85	2.81	0.04	2.83	2.79	2.84	0.05	2.82	−0.01
4.63	4.65	0.02	4.64	4.53	4.57	0.04	4.55	−0.09
4.40	4.59	0.19	4.50	4.53	4.78	0.25	4.66	+0.16
2.27	2.24	0.03	2.26	2.23	2.35	0.12	2.29	+0.03
4.85	4.97	0.12	4.91	4.97	4.91	0.06	4.94	+0.03
4.89	4.92	0.03	4.91	4.92	4.86	0.06	4.89	−0.02
4.07	4.14	0.07	4.11	4.14	4.14	0.00	4.14	+0.03
2.93	2.98	0.05	2.96	3.01	2.93	0.08	2.97	+0.01
6.34	6.32	0.02	6.33	6.32	6.34	0.02	6.33	0.00
4.91	4.97	0.06	4.94	4.90	4.92	0.02	4.91	−0.03
4.56	4.58	0.02	4.57	4.55	4.52	0.03	4.54	−0.03
3.68	3.65	0.03	3.67	3.79	3.70	0.09	3.75	+0.08
3.65	3.74	0.09	3.70	3.50	3.52	0.02	3.51	−0.19
2.79	2.84	0.05	2.82	2.76	2.83	0.07	2.82	0.00
	Av.	0.05			Av.	0.06	Av.	0.04

Discussion

The use of perchloric acid in digesting appreciable quantities of biological material results in a much more rapid method for phosphorus determinations than any hitherto presented. Results so obtained were accurate both in recovery of added

phosphorus and in determination of phosphorus in biological materials. The average difference in results by the two methods is, in most cases, less than the difference between duplicates by either method. Only in the case of the gravimetric determination on pasture grass, Table IV, is the difference greater. In the gravimetric analysis of fertilizer as shown in Table V, the difference between the two methods is less than between duplicates in either one. In all cases the difference is small.

Summary

In making phosphorus determinations on biological materials, the addition of perchloric acid during the sulfuric-nitric acid method of digestion decreases the time required for the digestion from hours to about 15 minutes. A water-clear solution is obtained. This method of digestion results in no loss and the phosphorus may be accurately determined on the solution volumetrically, gravimetrically, or colorimetrically without interference.

Acknowledgment

The author is indebted to H. L. Cole, assistant professor in chemistry, for his help during the earlier part of the problem, and to H. K. Murer, who is studying the Zinzadze method, for his help on that portion of this work.

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Recovery of Silver and Iodine from Silver Iodide

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The accumulation of a quantity of silver iodide-oxide residues, in methylation studies involving silver oxide and methyl iodide, necessitated the recovery of the silver and iodine. A survey of the available methods indicated the lack of any by which both free iodine and silver can conveniently be recovered.

Chlorine (*2*), hydrogen chloride (*1*), and ferric chloride (*4*) have been used to convert silver iodide to the chloride, but no mention of the use of aqua regia for this purpose could be found. Aqua regia (1 part of concentrated nitric acid to 3 parts of concentrated hydrochloric acid by volume) reacts smoothly and quantitatively with silver iodide to form the chloride. The reaction proceeds vigorously although not violently, without external heating and with the evolution of only a small amount of brown oxide of nitrogen. The silver iodide should be ground to pass a 40-mesh sieve and the mixture shaken frequently to hasten the reaction. In dealing with large quantities, or if the silver iodide is not finely ground, more than one treatment may be required to complete the transformation. After completion of the reaction the aqua regia is diluted with water to precipitate dissolved halides and the residue filtered and washed with water. The chloride is separated from unconverted iodide by shaking with concentrated ammonium hydroxide. If necessary, the treatment with aqua regia is then repeated until no residue remains upon shaking with ammonium hydroxide. Reduction of the silver ammonium chloride, in excess ammonium hydroxide, is accomplished by sodium hyposulfite as suggested by Firth and Higson (*3*).

The iodine monochloride, which is formed by the action of aqua regia in the process, is stable in the acid solution. Hydrolysis of the iodine monochloride, by which eight-tenths of the iodine is precipitated and two-tenths converted to iodic acid, is brought about by adding sodium hydroxide to the diluted aqua regia until it is just acid to litmus (*5*). In neutralizing the acid an excess of alkali must be avoided to prevent solution of some iodine. After filtration of the iodine, the mother liquor should be tested by adding more acid or alkali. If the correct acidity was not attained, this will cause additional iodine to precipitate. The remaining two-tenths of the iodine, in solution as iodic acid, is precipitated by the addition of the calculated amount of sodium hyposulfite solution. An excess must be avoided, otherwise iodine will be reduced further, yielding soluble sodium iodide. The calculation of the required amount of hyposulfite was based on Equation 5 given below. These two steps may be carried out in the same operation by adding the hyposulfite solution after the first precipitation of iodine. The acidity of the solution should again be adjusted after adding the hyposulfite. The iodine is recovered by filtration of the cold solution on a Büchner funnel, using a hardened paper. It is washed with ice water and dried in a desiccator over concentrated sulfuric acid.

In dealing with silver iodide-oxide residues, the silver oxide is removed by first extracting with dilute nitric acid. The silver iodide remains undecomposed and the dissolved silver is precipitated by reduction of its ammoniacal solution with sodium hyposulfite as in the case of silver ammonium chloride (*3*).

The reactions involved in this recovery process are represented by the following equations:

Conversion of silver iodide to chloride:

$$HNO_3 + 3HCl \longrightarrow Cl_2 + NOCl + 2H_2O \quad (1)$$

$$AgI + Cl_2 \longrightarrow AgCl + ICl \quad (2)$$

Hydrolysis of iodine monochloride:

$$ICl + H_2O \longrightarrow HCl + HIO \quad (3)$$

$$5HIO \longrightarrow 2I_2 + HIO_3 + 2H_2O \quad (4)$$

Reduction of iodic acid:

$$6HIO_3 + 5Na_2S_2O_4 + 2H_2O \longrightarrow 3I_2 + 10NaHSO_4 \quad (5)$$

The method was developed for the recovery of silver and iodine from residues, but in order to study the reaction pure silver iodide was employed, since it is the unreactivity of this substance which presents the difficulty in the procedure. A description of a typical experiment is given below and the method has been successfully employed starting with a 600-gram lot of silver iodide-oxide residues.

Experimental

Conversion of Silver Iodide to Chloride. To 75.0 grams (0.32 mole) of silver iodide (40-mesh) were added 61 ml. of con-

centrated nitric acid and 162 ml. of concentrated hydrochloric acid (sufficient to produce 0.64 mole of chlorine). The mixture, which at first darkened, was stirred for 5 minutes, at the end of which time the initial vigorous reaction had subsided. It was heated on the steam bath for 25 minutes with frequent shaking and then diluted with 250 ml. of distilled water and cooled in ice. The precipitate was filtered off, thoroughly washed with water, and dried to constant weight at 100° to 105° C. Calculated for AgCl: 45.80 grams. Found: 45.72, 45.50 grams.

Reduction of Silver Chloride to Silver. The silver chloride, obtained in the above-described experiment, was dissolved by shaking with 400 ml. of concentrated ammonium hydroxide. Solution was complete, but a small quantity of insoluble material gradually separated. This was filtered off and shaken with more ammonium hydroxide which dissolved it. To the filtered solution, which possessed a very slight turbidity, was added an excess of sodium hyposulfite solution. The precipitated silver was filtered, washed with water, and dried to constant weight at 100° to 105° C. Calcd. for Ag: 34.47 grams. Found: 33.07, 33.80 grams.

Recovery of Iodine. The diluted aqua regia from the above described experiment was cooled in ice and sodium hydroxide solution was added until just acid to litmus. A solution containing 9.3 grams of sodium hyposulfite was then added and the solution again made just acid to litmus. The precipitated iodine was filtered on a Büchner funnel, using a hardened paper. To the filtrate an additional small quantity of hyposulfite was added causing a little more iodine to precipitate. The calculated amount is not quite sufficient, probably because of the oxidizing action of some chlorine or hypochlorous acid which is present. This iodine was added to the first portion which was washed with ice water, filtered, and dried in a desiccator over concentrated sulfuric acid for 36 hours. Calculated for I_2: 40.54 grams. Found: 39.12 grams.

In another similar experiment the iodine was filtered off before the addition of the sodium hyposulfite solution. To the faintly acid (to litmus) filtrate was added a solution containing an excess of barium nitrate. The solution was allowed to stand overnight, cooled in ice, and the barium iodate filtered off. The precipitate was washed with dilute hydrochloric acid followed by water, and dried to constant weight at 110° to 115° C. Calculated for $Ba(IO_3)_2.H_2O$: 16.16 grams. Found: 16.92 grams.

Summary

Silver and iodine are obtained from silver iodide in a process involving the conversion of the iodide to the chloride by means of aqua regia. Iodine monochloride is formed, which is hydrolyzed to free iodine and iodic acid. The iodic acid is reduced to iodine with sodium hyposulfite. The silver chloride is dissolved in ammonium hydroxide and the silver ammonium chloride thus formed is subsequently reduced by sodium hyposulfite.

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Improved Gas Burner Top for Ignition in Determination of Potash in Fertilizers

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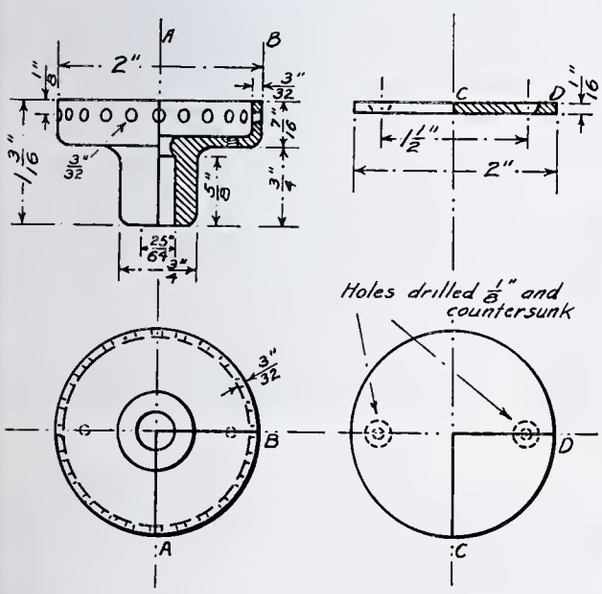

Figure 1. Potash Burner

Cast of soft gray iron. Hole in stem drilled 25/64 inch, leaving shoulder as indicated. 24 radial holes drilled 3/32 inch diameter at 20° to horizontal.

Figure 2. Photograph of Burner

Metal cylinder may be placed around burner to avoid interference with drafts and aid in heating sides of dish.

The danger of losses when ignition is carried out at too high temperatures in the determination of potash in fertilizers has been shown by Lockhart (*2*). A special burner top has been designed which fits the ordinary Bunsen burner (Figure 1), and by means of which it is possible to heat the dish gradually at a low temperature on the sides as well as the bottom (Figure 2). After preliminary heating on this burner it is necessary to heat to dull redness for a few seconds on a Meker burner.

Kraybill and Thornton (*1*) have shown that ignition with this type of burner gives higher and more uniform results than ignition with the Meker burner. The authors have used this burner top in routine analyses of fertilizers during the last year and find that the use of a battery of these saves much time and yields accurate and uniform results.

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Employment of Potassium Ferrocyanide in Standardization of Dilute Potassium Permanganate

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In the process of applying permanganimetry to microchemical analysis, a more convenient standard than sodium oxalate seems desirable. When employing 0.01 N potassium permanganate in analytical procedures, frequent standardizations are essential. Although sodium oxalate has proved to be accurate for the purpose, it has the disadvantage of having to be freshly prepared. Potassium ferrocyanide is a good reducing agent, which is very stable in properly prepared solutions; is obtainable in a high degree of purity; has a high equivalent weight (an error of 37 mg. in weighing one equivalent of the anhydrous salt would cause an error of only 0.01 per cent); and does not require heat for titration against potassium permanganate.

Table I. Comparative Standardization of Potassium Permanganate

	Normality of $KMnO_4$ Against $K_4Fe(CN)_6$	Normality of $KMnO_4$ Against $Na_2C_2O_4$[a]	Average Difference %
Weighing buret	0.009741	0.009723	
	0.009736	0.009719	
	0.009739	0.009750	0.08
	0.010557[b]	0.010566[b]	0.09
10-cc. buret	0.01274	0.01275	
	0.01275	0.01275	0.02
	0.01275	0.01275	
	0.01052[b]	0.01051[b]	0.10
	0.01280[b]	0.01280[b]	0.00
5-cc. buret	0.01051	0.01050	
	0.01050	0.01051	
	0.01051	0.01054	0.10
	0.01285[b]	0.01286[b]	0.08
	0.01041[b]	0.01043[b]	0.19

[a] Sodium oxalate titrations were carried out in the concentrations recommended by McBride (*8*). Good results were also obtained with arsenic trioxide according to the method of Lang (*7*).
[b] Average of three or more titrations.

The employment of potassium ferrocyanide as a primary standard for potassium permanganate was first suggested by de Haen (*1*) in 1854. Since then it has been suggested repeatedly for this purpose by many investigators, but has not gained popularity because of the difficult end point. Potassium ferrocyanide is a component of a reversible oxidation-reduction system which lends itself well to potentiometric titration with potassium permanganate (*5*, *9*) and to titration with permanganate in the presence of suitable oxidation-reduction indicators (*3*, *4*). The latter articles by Knop and his co-workers deal with the use of the dye, erioglaucine, as such an indicator.

Although Kolthoff (*5*), using potentiometric methods, had shown that the reaction between ferrocyanide and permanganate was quantitative, even in very dilute solutions, Knop and Kubelkova (*4*), in attempting to use potassium ferrocyanide with erioglaucine as the indicator for the standardization of 0.005 N permanganate, obtained unsatisfactory results which they ascribed to the action of light and lack of knowledge as to the exact conditions of the titration.

Dilute solutions of potassium permanganate (0.01 N) are usually prepared by the dilution of more concentrated standard solutions or by standardization against 0.01 N sodium oxalate. The former method has been questioned by Halverson and Bergeim (*2*) and the latter method is laborious and time-consuming. An investigation into the conditions of standardization against dilute potassium ferrocyanide, using erioglaucine as an indicator, confirmed Knop's observations as to the excellence of the end point. The change from apple-green to amber is sharp and unmistakable even in artificial light. One hundred routine titrations, selected at random, showed a standard deviation of ±0.0017 cc. when carried out under the following conditions:

The sulfuric acid concentration at the end of the titration should not be less than 0.1 N or more than 1.0 N. The final volume should not be greater than 50 cc. The temperature should not exceed 40° C. Titrations should be carried out rapidly with continuous agitation.

That such titration figures are quite valid is shown by comparative standardization of dilute permanganate against both sodium oxalate and potassium ferrocyanide (Table I). An indicator correction must be applied to the potassium ferrocyanide titer. The work of Kolthoff and Pearson (*6*) with regard to the stability of solutions of potassium ferrocyanide has been confirmed and extended (Table II). Because of the stability of the standard and the convenience of the titration, this method offers a considerable saving of time and labor over the commonly used oxalate method for the routine standardization of potassium permanganate.

Table II. Stability of Dilute Potassium Ferrocyanide Solutions

(Solutions were prepared from water distilled from permanganate, stored in brown bottles, and kept in the dark. Room temperature fluctuated from 20° to 35° C. Sodium carbonate concentration was 0.2 per cent in all cases.)

Original Normality	Age *Days*	Change in Normality	Change %
0.010878	22	−0.000003	0.03
0.008744	27	−0.000009	0.10
0.010222	176	−0.000009	0.09
0.010000	216	−0.000012	0.12

Experimental

All volumetric and gravimetric apparatus had been recently calibrated. A 5-ml. buret, graduated in 0.01-ml. divisions (which could be estimated to 0.001 ml. with the aid of a reading glass) and equipped with a platinum-iridium tip, as described by Shohl (*10*), was used for the determination of the end-point correction and routine standardization. For larger volumes a 10-ml. buret and a weighing buret were used. Sodium oxalate was obtained from the U. S. Bureau of Standards. Potassium ferrocyanide, purified by recrystallization from hot water, or Kahlbaum's "guaranteed" grade was used. Potassium permanganate was prepared by the Halverson and Bergeim procedure (*2*).

Preparation of Potassium Ferrocyanide Solutions. Heat powdered $K_4Fe(CN)_6.3H_2O$ in a tared weighing bottle to constant weight at 106° C. and make up to volume in 0.2 per cent sodium carbonate solution. The equivalent weight of the anhydrous salt is 368.3. Store in brown bottles and protect from light.

METHOD OF STANDARDIZATION OF 0.01 *N* POTASSIUM PERMANGANATE. To each cc. of 0.01 *N* potassium ferrocyanide add 2 cc. of *N* sulfuric acid and titrate with 0.01 *N* potassium permanganate in the presence of 0.05 cc. of 0.1 per cent aqueous erioglaucine. Subtract an end-point correction of 0.012 cc. from the titer for each 0.05 cc. of erioglaucine. (The authors' samples of this dye showed no deterioration on long standing.)

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Separation and Detection of Cyanide

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HYDROGEN cyanide is rapidly displaced when an inert gas is bubbled through its aqueous solution. Utilizing this fact, Chelle[1] described an apparatus in which the acid is separated by means of a stream of carbon dioxide-free air and caught in alkali; in the alkali solution the test for cyanide is subsequently made. This paper describes a simpler and much more convenient set-up, though employing the same principle, which is particularly useful for the detection of cyanide in highly insoluble cyanides, in solid mixtures containing carbonate, and in sodium carbonate solution.

The apparatus (Figure 1) consists of two 15 × 180 mm. test tubes and a 100-cc. Erlenmeyer flask connected by rubber and glass tubing as indicated. Two-tenths gram of the substance to be analyzed for cyanide (or 3 cc. of a prepared solution, made by treating 3 grams of the substance with 50 cc. of 1.5 *M* sodium carbonate, boiling for 3 minutes, and filtering) is introduced into the flask. The first test tube contains 6 cc. of 3 *M* hydrochloric acid, and the second, 10 cc. of 6 *M* sodium hydroxide. A plug of absorbent cotton in the neck of the flask prevents any of the liquid from being carried over into the alkali. By slowly turning on the compressed air, the acid in the first test tube is forced over into the flask. A slow stream of air is then allowed to bubble through the flask for 30 minutes. Any cyanide in the mixture is thus carried over into the second test tube, where it is absorbed by the alkali. It is detected in this solution by means of the Prussian blue reaction carried out as follows: To the alkaline solution are added a few drops of a freshly prepared 1 *M* ferrous sulfate solution, the mixture is heated almost to boiling and then thoroughly cooled. The solution is then carefully neutralized with 12 *M* hydrochloric acid and a few drops of 1 *M* ferric chloride solution are added. The formation of a blue precipitate or, with very small amounts of cyanide, of a blue or blue-green coloration indicates the presence of cyanide.

EXPERIMENTAL

Following the proposed method, 0.2 mg. of cyanide as sodium cyanide in 3 cc. of 1.5 *M* sodium carbonate yields a decided positive test. With large amounts of cyanide (10 to 100 mg.) the separation of the acid, although not quite complete in 30 minutes, is sufficient to yield a very large Prussian blue precipitate, proportional to the amount of cyanide present.

EFFECT OF OTHER VOLATILE ACIDS. The presence of large amounts of carbonate as sodium carbonate (3 cc. of 1.5 *M* sodium carbonate containing 0.5 gram of the anhydrous salt) offers no interference. Similarly, sulfite and thiosulfate have no disturbing effect, for, with a mixture of 1 mg. of cyanide as sodium cyanide and 0.2 gram of Na_2SO_3 or $Na_2S_2O_3 \cdot 5H_2O$, an excellent test for cyanide was obtained. In mixtures containing sulfide, the test is complicated by the precipitation of ferrous sulfide when ferrous sulfate is added and by the separation of sulfur upon the addition of ferric chloride. However, a satisfactory final test is obtained if the solution, after the addition of ferrous sulfate and acidification, is boiled for one minute to expel the greater part of the hydrogen sulfide and then treated with ferric chloride. In this way a test for cyanide was obtained in a mixture of 1 mg. of cyanide as sodium cyanide and 0.2 gram of finely powdered ferrous sulfide. In the presence of nitrite the separation and tests for cyanide fail, doubtless because of oxidation of the cyanide.

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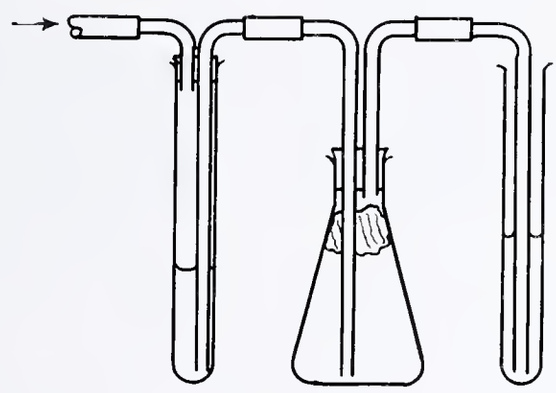

FIGURE 1

INTERFERING ACIDS. The Prussian blue test cannot be directly applied to mixtures containing ferrocyanide, ferricyanide, or thiocyanate. These acids, however, cause no interference in the proposed method, since excellent controls were obtained when 0.2 gram of potassium ferrocyanide, ferricyanide, and thiocyanate were separately analyzed.

TABLE I. TEST FOR CYANIDE

SUBSTANCE	AIR DISPLACEMENT		PRUSSIAN BLUE TEST
	0.2 gram of solid	3 cc. of prepared soln.	3 cc. of prepared soln.
$Zn(CN)_2$	+	+	Doubtful[a]
$Ni(CN)_2$	Faint[b]	+	Doubtful[c]
$Pb(CN)_2$	+	+	+
AgCN	+	−	−
CuCN	+	+	Faint
$HgO.Hg(CN)_2$	+	+	−[d]

[a] Large bluish white precipitate, probably $Zn(CN)_2$ or $Zn_2Fe(CN)_6$.
[b] Indicating less than 1 mg. of cyanide.
[c] Greenish white precipitate, probably $Ni_2Fe(CN)_6$.
[d] Heavy brown precipitate, probably mercury formed by reduction with $FeSO_4$. Mercuric cyanide also yields the same confusing result by direct test. Like the oxycyanide, it yields a satisfactory cyanide test by the air-displacement method.

INSOLUBLE CYANIDES. The common insoluble cyanides (all commercial products) and their prepared solutions were tested for cyanide by the air-displacement method, with the results indicated in Table I. For comparison, the Prussian blue test was applied directly to the prepared solution of each of the substances, in accordance with the normal procedure if ferrocyanide, ferricyanide, and thiocyanate were known to be absent.

With the exception of nickel cyanide all the common insoluble cyanides tested respond to the cyanide test when subjected to the authors' procedure. Only in the case of silver cyanide does the method fail when applied to the sodium carbonate prepared solution, for the reason that the salt is not transposed by the carbonate treatment. It is particularly noteworthy that only lead cyanide responds to the direct Prussian blue test. It is thus evident that the separation must be carried out even when the interfering acids are definitely known to be absent.

Summary

A method for the detection of cyanide is proposed that depends upon the separation of the acid by air displacement in a simple apparatus, followed by the application of the Prussian blue test. The method is sensitive to 0.2 mg. of cyanide and is applicable in the presence of ferrocyanide, ferricyanide, thiocyanate, carbonate, sulfite, thiosulfate, or sulfide.

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A Simple Photoelectric Thermoregulator

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In the course of work on the catalytic oxidation of organic substances at temperatures between 100° and 500° C., it was found necessary to develop a simple and inexpensive device for the automatic control of temperature, in order to obtain reproducible results with the minimum expenditure of time.

Various temperature-controlling devices (*1–12*) utilizing either photoelectric cells or thyratron tubes have appeared in the literature during the past few years. However, all these employ very elaborate or expensive auxiliary apparatus such as mirror galvanometers and other instruments of high precision, the use of which is impractical in an ordinary chemical laboratory where fumes and other corrosive substances are always to be found. Furthermore, these devices frequently require complex optical systems, often necessitating a large amount of permanent wall or desk space.

The present device has been found highly suitable in certain catalytic reactions where greater accuracy of temperature control than ±0.25° is unnecessary. It is to be recommended for its compactness, efficiency, and comparatively simple and inexpensive construction. Instead of a mirror galvanometer, it employs a Leeds & Northrup potentiometer indicator. This type of instrument, it is true, represents some outlay of money, but is found in most chemical laboratories for the measurement of temperature. Since its use as an auxiliary apparatus does not in any way impair its customary utility, its initial cost may be disregarded, and the cost of the thermoregulator will not be more than $15 to $20.

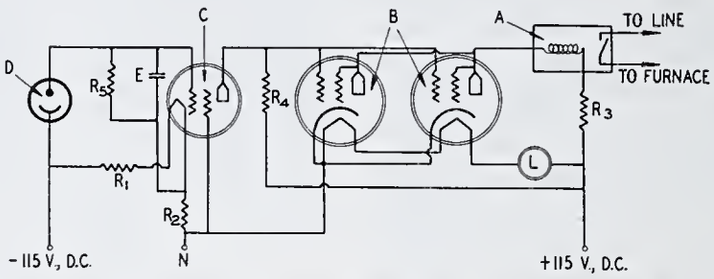

Figure 1. Direct Current 230-Volt Thermionic Relay

A. G. E. 110-volt, 60-cycle relay, type C. R. 2810-1265-G1. A thin sheet of mica should be interposed between the iron core of the solenoid and the control arm of this relay. This seems to be effective in preventing sticking of the contacts.
B. 48-Type vacuum tube
C. 22-Type vacuum tube
D. PJ 22-Photoelectric cell
E. 0.002-Mfd. condenser, foil type
L. 60-Watt, 115-volt tungsten filament G. E. Mazda lamp used as a convenient resistant
R_1 and R_3. 500-Ohm resistors
R_2. 400-Ohm resistor. Although it might be best to have R_1 and R_2 variable, this specification is not absolutely necessary.
R_4. Grid leak, 1 megohm
R_5. Grid leak, 50 megohms

In the construction of the authors' device, a vertical slit 2 mm. wide and 8 mm. long is cut through the bottom of the galvanometer of a Leeds & Northrup double-range potentiometer indicator, No. 8657C, just to the left of the zero point on the scale. This slit admits light to the compartment ordinarily occupied by a dry cell, which is removed to an outside position and its place taken by a photoelectric cell. A strip of black paper slightly larger than the dimensions of the slit and pointed at its forward end is pasted on to the galvanometer needle which, with increasing temperature, moves to the left of the zero mark as the e. m. f. of the thermocouple rises above that set on the potentiometer. In so doing, it cuts off the light falling on the photoelectric cell which, by a suitable amplification, operates a sensitive relay, thereby bypassing a part of the current through additional resistance. As the temperature of the furnace decreases, the opposite effect is produced—e. g., the galvanometer needle moves to the right, thereby exposing the photoelectric cell to the light source which is most conveniently provided by a 40-watt 110-volt desk lamp placed about 20 cm. (8 inches) above the slit.

The photoelectric cell with the system of amplification and sensitive relay is shown diagrammatically in Figure 1. The entire apparatus is assembled in a ventilated cabinet in which the dry cell for the potentiometer may also be placed.

In operation the pointed tip of the paper-covered gvaalnometer needle is adjusted so as to balance on the zero point on the scale immediately to the right of the slit. The furnace temperature is adjusted by variable resistance 10° to 15° higher than that desired. Too high a temperature must be avoided, since the lag created drives the galvanometer needle completely across the slit, thereby again turning on the current.

The present device has been tested using a single-junction chromel-alumel thermocouple and a well-insulated furnace over a range from 100° to 500° C., and it has been found to control the temperature to within ±0.5° C. Under the same conditions a tri-junction thermocouple increased the accuracy to within ±0.25° C., which is about the limit of accuracy of the potentiometer used. The accuracy obtained in any case would also depend upon the lagging of the furnace employed.

Although the present thermoregulator has been found highly suitable in catalytic reactions, it could be used to control the temperature of any chemical reaction. Furthermore, its range should not be confined to temperatures between 100° and 500° C.

Acknowledgment

It is a pleasure to acknowledge the valuable suggestions and assistance rendered by Ralph D. Bennett of the Department of Electrical Engineering.

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Determination of Uric Acid in the Mixed Excrement of Birds

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AN ACCURATE analysis of the feces is essential for the calculation of digestion coefficients. It is difficult to obtain the necessary data in the case of birds because the urine and the feces are mixed in the cloaca and excreted together; a method for differentiating the urinary constituents from the fecal constituents present in the mixed excrement is necessary if one is to obtain data for measuring digestibility.

In general, the methods used to study digestion in poultry are based on either of two principles. The first is to alter the bird by surgical means so that the urine and the feces are voided separately. The second is to make a chemical estimation of the constituents excreted only in the urine or only in the feces.

The protein digestion and metabolism of birds can be studied if we are able to measure the amounts of nitrogen excreted in the forms of uric acid and ammonia, which are the chief end products of nitrogen metabolism in birds. Uric acid is excreted only in the urine. Some ammonia is excreted in the feces, and Katayama (*5*) introduced a factor to correct for the small amount which is normally present. Not all the urinary nitrogen is present in the forms of uric acid and ammonia (*3–5*). Therefore, it is necessary to apply a correction factor to the sum of the uric acid nitrogen and the ammonia nitrogen to obtain the total urinary nitrogen. The various formulas developed to calculate the partition of the excrement nitrogen can be expressed in the following general forms:

1. Fecal nitrogen = excrement nitrogen − k (uric acid nitrogen + ammonia nitrogen)

k is a constant to correct for ammonia nitrogen in the feces and for the urinary nitrogen not present in the forms of uric acid and ammonia.

2. Urinary nitrogen = excrement nitrogen − fecal nitrogen

Working with Katayama's data, Titus (*11*) found that the following modification of Equation 1 gave less variable results than the original form:

Fecal nitrogen = 0.9784 excrement nitrogen − 1.0253 uric acid nitrogen − 1.2641 excrement ammonia nitrogen − 0.0554

In order to use these formulas one needs an accurate method for the determination of uric acid in the mixed excrement of fowls. Several methods, based upon different principles, are reported in the literature. Considerable difficulty was experienced by Brown (*2*), Bartlett (*1*), Katayama (*5*), St. John (*7*), and other workers who attempted to use the methods previously recorded in the literature. All the methods give good results when tested on pure uric acid, but are not so rapid and accurate when used on excrement samples. There is a real need for an accurate and convenient method for the determination of uric acid in excrement.

The writer has subjected a number of these methods to critical tests with a view to selecting or developing an accurate and rapid technic for the determination of uric acid in the mixed excrement of fowls. The following methods have been studied:[1]

Brown's isolation and piperidine titration (*2*).
Brown's method, modified to recover the uric acid gravimetrically instead of titrating it.
Katayama's method for separating the uric acid in the form of ammonium urate, converting it back to the acid form, and then determining nitrogen by the Kjeldahl method (*5*).
Katayama's method modified for gravimetric recovery of the isolated uric acid.
Kionka's piperidine titration (*6*).
St. John's method for isolating uric acid (*7*).
Suzuki's method for measuring the amount of ammonia required to convert the uric acid into ammonium urate (*10*).
Woodman's method for isolating uric acid (*12*).
The writer's differential extraction method, which is based on the assumption that acidified water extracts the same nitrogenous constituents, with the exception of uric acid, as does piperidine.

DIFFERENTIAL EXTRACTION METHOD

Weigh out two equal samples of the excrement. Two grams make a convenient quantity to handle. To each sample add 20 cc. of a hydrochloric acid solution (5 parts of the concentrated reagent and 95 parts of water), and let the samples stand overnight. This treatment converts urates into free uric acid. Filter, and wash each residue with about 25 cc. of cold water. Transfer the residues, plus the filter papers, to their respective original beakers. To one of the residues add sufficient piperidine to make the mixture distinctly alkaline to phenolphthalein. Bring the volume to approximately 25 cc. with distilled water. To the other residue add a similar quantity of 0.1 N hydrochloric acid. Digest both mixtures in a water bath at 60° C. for 1 hour.

Filter each mixture through a layer of Celite on a filter cloth (the filter cloth recommended by the Association of Official Agricultural Chemists for use in the determination of crude fiber is satisfactory), and wash the residues with equal quantities of cold wash water. Continue washing until the wash water from the piperidine-extracted material is free from an alkaline reaction. Transfer the residue (and Celite) from the piperidine extraction to a Kjeldahl flask for a total nitrogen determination, A. Transfer the residue (and Celite) from the water extraction to a second Kjeldahl flask for a total nitrogen determination, B.

$B - A$ = uric acid nitrogen
Uric acid nitrogen × 3 = uric acid

[1] Since this work was completed, another method for determining fecal nitrogen has been reported in the literature. Stotz (*8, 9*) has described a method for oxidizing uric acid by nitric acid, and washing out the resulting soluble products. After applying suitable corrections, the remaining nitrogen can be considered as fecal nitrogen.

Plan of Tests

Each method was tried first on known amounts of chemically pure uric acid, and if uniform and accurate results were obtained, the method was then applied to a standard sample of droppings. This standard sample consisted of a large quantity of droppings from adult Rhode Island Red cocks, dried, well mixed, and finely ground to provide a uniform sample on which to test the methods. If the results justified further study, known amounts of pure uric acid were added to weighed samples of the excrement and the mixture was analyzed for uric acid. The percentage of the added uric acid which was recovered was considered to be an indication of the accuracy of the method.

A summary of the results of the tests is shown in Table I. The highest and the lowest values obtained on the standard sample of excrement are given to indicate the variation in the results obtained with each method.

erably lower results than any, but one, of the other methods tested. This is contrary to what one might expect from the relative ability of the methods to determine uric acid, alone or when added to excrement. Several experiments were made in the hope that they would offer some explanation for this discrepancy.

A synthetic sample was prepared to contain a known amount of uric acid. Besides the uric acid this sample contained urea, sodium chloride, ammonium chloride, sucrose, and gelatin. The differential extraction method gave a more accurate measure of the amount of uric acid present in this synthetic sample than did any other of these methods.

When the xanthoproteic test is made on the material extracted by solvents used in the methods of Brown, Katayama, St. John, and Woodman, a positive reaction is noted. Pure uric acid does not give this color reaction. Therefore, these methods must extract nitrogenous substances other than uric

Table I. Summary of Tests of Methods for Determining Uric Acid in Mixed Excrement of Birds

Method	Recovery of c. p. Uric Acid		Uric Acid in Standard Sample of Excrement			Recovery of Added c. p. Uric Acid in Presence of Excrement	
	No. of detns.	Av.	No. of detns.	Range	Av.	No. of detns.	Av.
		%		%	%		%
Brown	50	96.8	47	10.60–12.32	11.55	20	59.6
Brown with gravimetric recovery	18	99.1	38	9.37–13.16	11.32	19	70.4
Katayama	21	96.5	20	7.57– 9.57	8.88	Inconsistent and low	
Katayama with gravimetric recovery	26	97.7	..	...	...	..	..
Kionka	21	97.2	Analysis impossible—heavy pigmentation				
St. John	21	94.7	9	11.43[a]–14.18[a]	13.02[a]	18	50.2
Suzuki	23	99.9	40	10.14–14.48	11.73	22	92.9
Woodman	54	96.5	42	9.97–13.30	11.76	2	14.5
Differential extraction	20	99.1	26	8.10–10.18	8.89	74	93.8

[a] This is not the standard sample which was used in the determinations by the other methods.

For the recovery of uric acid in the presence of excrement, two equal samples of the excrement were taken. To one of these a known amount of pure uric acid was added. Then the total uric acid was determined in each sample, and the difference in the results was the portion of the added uric acid which was recovered.

Discussion of Methods

Numerous objections, either theoretical or practical, may be raised about each of the methods tested. The writer has found that all efficient solvents of uric acid have a destructive action upon the acid itself, but this can be minimized by leaving the uric acid in solution for as short a time as possible. The extreme difficulty in filtering the alkaline solution, presumably because of the colloidal material present in the excrement, complicates the rapid removal from the solvent. The most successful method for speeding the filtration was to freeze the alkaline uric acid solution with the suspended insoluble matter, and then to filter with suction while the material melted.

Suzuki's method and the differential extraction method are free from errors attributable to the destruction of uric acid by alkaline solvents, because they do not depend upon isolating and measuring the uric acid as such.

Titration of uric acid with either piperidine or potassium permanganate was considered impractical, because in all cases the end points were indistinct. Heavy pigmentation of the solution interfered with the colors that indicated the end points of the titrations.

The most accurate measurements of pure uric acid, either alone or when added to excrement samples, were obtained with Suzuki's method and with the differential extraction method.

The average values for the per cent of uric acid present in the standard sample of excrement varied with the different methods. The differential extraction method gave considerably lower results than any, but one, of the other methods tested. This is contrary to what one might expect from the relative ability of the methods to determine uric acid, alone or when added to excrement. Several experiments were made in the hope that they would offer some explanation for this discrepancy.

A synthetic sample was prepared to contain a known amount of uric acid. Besides the uric acid this sample contained urea, sodium chloride, ammonium chloride, sucrose, and gelatin. The differential extraction method gave a more accurate measure of the amount of uric acid present in this synthetic sample than did any other of these methods.

When the xanthoproteic test is made on the material extracted by solvents used in the methods of Brown, Katayama, St. John, and Woodman, a positive reaction is noted. Pure uric acid does not give this color reaction. Therefore, these methods must extract nitrogenous substances other than uric acid. This phenomenon may account for the high values obtained with the isolation methods.

After considering the results of these tests, the writer is inclined to place more confidence in the lower values obtained on the standard sample. The differential extraction method is very simple, and presents no difficulties in manipulation. For this reason the writer believes that it offers some distinct advantages over any other method which has been proposed.

Summary and Conclusions

Nine different procedures for the determination of uric acid in the mixed excrement of birds have been tested. None of the methods reported in the literature yielded satisfactory results.

A differential extraction method proposed by the writer is recommended because of its simplicity and accuracy. Two equal samples of excrement are extracted, one by piperidine and the other by acidified water. The difference in unextracted nitrogen is considered to be uric acid nitrogen.

Acknowledgment

The author wishes to thank Harry W. Titus of the Bureau of Animal Industry for valuable suggestions made in connection with this study.

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Benzoyl Auramine G

A New Indicator for Kjeldahl Nitrogen Determinations

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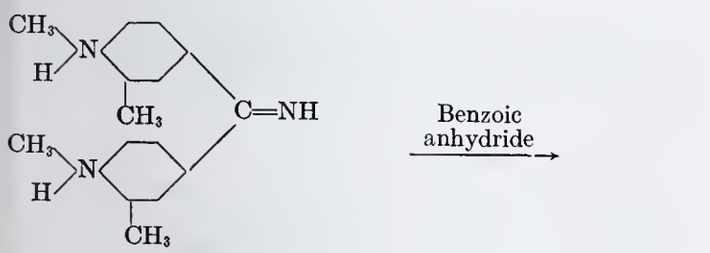
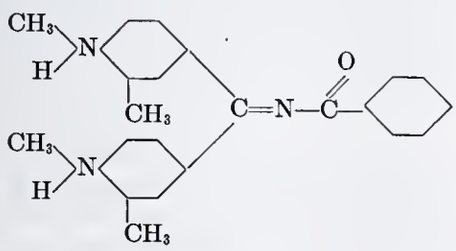
THE indicators recommended by the Association of Official Agricultural Chemists for use in the determination of nitrogen by the Kjeldahl method are methyl red (pH range 4.4 to 6.0) and cochineal (pH range 4.8 to 6.2). Methyl orange is occasionally used, but its pH range of 2.9 to 4.0 is somewhat too low to be satisfactory. Each of these three indicators changes from red to yellow, with an intermediate orange color, and there is often a difference of opinion between individuals as to the exact end point.

A new indicator, benzoyl auramine G, which is somewhat more satisfactory than any of these, is obtained by benzoylating the free base of auramine G [Colour Index No. 655 (*8*), Schultz (7th ed.) No. 752 (*6*)], which is the hydrochloride of 4,4′-dimethyldiamino-3,3′-dimethylbenzophenonimine, and is used in textile dyeing [not to be confused with the more common auramine O, a homologous dye (Colour Index No. 656, Schultz (7th ed.) No. 753)].

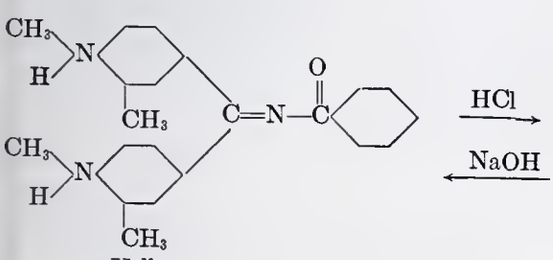


Auramine G base

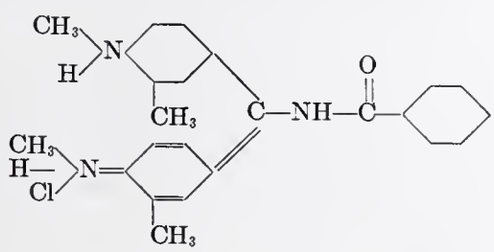


Benzoyl auramine G

Upon the addition of acid to this benzoyl derivative, its color changes very sharply from pale yellow to intense violet. This color change in similar compounds was attributed by Semper (*7*) to salt formation on one of the amino nitrogen atoms and conversion of one of the nuclei from the benzenoid to the quinoid form:



Yellow

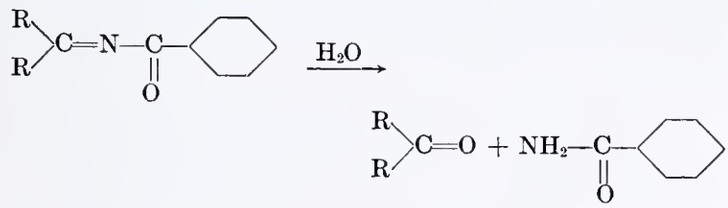


Violet

The quinoid form exhibits marked dichroism. In concentrated solution or in a deep layer it is red-violet, while in dilute solution or in a thin layer it is blue.

Benzoyl auramine G is particularly suitable for use in the Kjeldahl nitrogen determination method. Its color change is sharp. A complete change from intense violet to pale yellow (almost colorless) can be effected by the addition of two drops (0.07 cc.) of 0.1 *N* alkali. The actual end point, a change from blue to pale yellow, can be unmistakably observed upon the addition of less than a drop of 0.1 *N* alkali. The contrast between the two colors assists materially in the observation of the end point. This sharp change is due to the shortness of the pH range, pH 5 to 5.6, which is very nearly that of the concentrations of ammonium chloride usually encountered in Kjeldahl titrations—from 0.3 to 1.0 gram in from 100 to 300 cc. of solution (*5*).

A disadvantage in the use of benzoyl auramine G is the fact that it hydrolyzes (*3*):



In neutral solutions at room temperature this hydrolysis proceeds very slowly, but the rate of hydrolysis increases rapidly with increase in hydrogen-ion concentration or elevation of temperature. A similar effect is obtained on the alkaline side, but it is less pronounced. The indicator, therefore, should not be added to any solution until it is ready to be titrated, and the titration should then be completed without further delay. The effect of the products of hydrolysis upon the analytical results is negligible, since they are practically neutral and only a very small quantity of indicator is necessary. Good results were obtained with 3 to 7 drops (about 0.15 cc.) of a 0.25 per cent solution in methyl alcohol.

When the titration is carried out in daylight an intermediate gray color occurs between the violet and the yellow, indicating a pH of 5.4. By tungsten lighting, however, the quinoid form appears red, and hence the intermediate gray color is not observed; instead, the color is pale red just before the change to yellow. This color change is as readily observed as the other, and the indicator can therefore be used by artificial light as satisfactorily as by daylight.

Experimental

The indicator was prepared by a modification of the method used by Finckh and Schwimmer (*3*) in preparing a similar derivative of auramine O.

Preparation of Auramine G Base. To 3500 cc. of water were added 25 grams of commercial auramine G and 125 cc. of benzene, and the mixture was agitated by means of an efficient mechanical stirrer. An excess of ammonium hydroxide was added and the stirring continued for 15 minutes. The benzene layer was then separated and the aqueous layer extracted with a second 125-cc. portion of benzene. The combined benzene solutions were dried with sodium sulfate and evaporated to dryness at room temperature under a current of air. The residue was dried *in vacuo* over calcium chloride. The yield was 11 grams.

Benzoylation of Auramine G Base. A 10-gram sample of the base was dissolved in 60 cc. of benzene, a solution of 8.5

grams of benzoic anhydride (free from benzoic acid) in 40 cc. of benzene was added, and the mixture was refluxed for 5 hours. When cool, any precipitate was removed by filtration and the filtrate was mixed with 150 cc. of petroleum ether (b. p. 30° to 65° C.) and allowed to stand overnight. The product, which precipitated as a heavy liquid, was separated and washed twice with small amounts of petroleum ether. These washings were rejected. The product was then boiled with two or three successive 50-cc. portions of ethyl ether and, after 50 cc. of petroleum ether were added to each, they were allowed to stand overnight. The residual red liquid or gum, which consisted mostly of auramine G benzoate, contained little of the benzoyl derivative and was discarded. The product, which crystallized from the ether extracts as a mixture of a red gum and clusters of light yellow crystals, was separated by decantation, washed with petroleum ether, and recrystallized from chlorobenzene, from which it separated in small yellow needles. All the washings, except those previously indicated, were combined, and a second crop of pure product was obtained by recrystallizing the resulting precipitate from chlorobenzene.

Yield, first crop, 1.35 grams; second crop, 1.15 grams. Melting point, 176° to 177° C.

Total yield, 2.5 grams, 9 per cent of the theoretical.

Analysis: Calculated for $C_{24}H_{25}N_3O$: N, 11.32 per cent. Found: N, 11.14, 11.20 per cent.

Determination of pH Range of Benzoyl Auramine G. Two series of buffer solutions were used, the potassium acid phthalate-sodium hydroxide mixtures (*1*) and the McIlvain disodium phosphate-citric acid mixtures (*2*) checked electrometrically with a quinhydrone electrode. The results obtained with the McIlvain buffers are given in Table I. The other series gave identical results. The range of benzoyl auramine G is pH 5 to 5.6.

Table I. Color Change of Benzoyl Auramine G with Change of Hydrogen-Ion Concentration

Buffer[a] 0.2 *M* Na_2HPO_4	Buffer[a] 0.1 *M* citric acid	pH	Color of Solution: Daylight	Color of Solution: Tungsten light
Cc.	*Cc.*			
9.86	10.14	4.8	Intense violet	Intense red
10.30	9.70	5.0	Intense violet	Intense red
10.72	9.28	5.2	Pale violet	Light red
11.15	8.85	5.4	Gray	Pale red
11.60	8.40	5.6	Pale yellow	Pale yellow
12.09	7.91	5.8	Pale yellow	Pale yellow

[a] For each 10 cc. of buffer solution, a 0.2-cc. portion of a 0.04 per cent solution of the indicator in methyl alcohol was used.

Table II. Decomposition of Benzoyl Auramine G at Room Temperature in 0.04 Per Cent Solution in Methyl Alcohol

Time Elapsed	Extinction Coefficient *E* Layer Thickness 1 Cm.[a] 560 mμ	580 mμ	Relative Concentration Benzoyl Auramine G	Absorption Ratio $\frac{E\ 560}{E\ 580}$
Days				
0	1.21	1.22	1.00	0.99
3	0.95	0.96	0.78	0.99
17	0.90	0.92	0.74	0.98
24	0.85	0.86	0.70	0.99
31	0.84	0.84	0.69	1.00
67	0.64	0.64	0.53	1.00
90	0.56	0.56	0.46	1.00

[a] For these spectrophotometric measurements 1.5-cc. portions were withdrawn at the stated intervals and diluted to 100 cc. with methyl alcohol and 10 cc. of glacial acetic acid.

Determination of Rate of Decomposition. A 0.04 per cent solution of the indicator in methyl alcohol was prepared. Immediately after it was made up a 1.5-cc. portion of this solution was diluted with about 75 cc. of methyl alcohol, 10 cc. of glacial acetic acid were added, the solution was diluted with methyl alcohol to exactly 100 cc., and the absorption at suitable wave lengths determined. This was considered as the initial concentration. The relative concentrations found by subsequent examinations at the stated intervals are given in Table II. After the first rapid decline, the rate of decomposition slowed down, so that the concentration of the 3-month-old solution was slightly less than half of the original value and was still usable. The constancy (within experimental error) of the absorption ratio (*4*) shows that the change is quantitative and not qualitative.

Benzoyl Auramine G as an Indicator

An approximately 0.1 *N* solution of sodium hydroxide was standardized against pure benzoic acid, and the normality of a similar hydrochloric acid solution was determined by comparison, using bromothymol blue as the indicator. The two solutions were then similarly compared using benzoyl auramine G and methyl red in the presence of two different concentrations of ammonium chloride. The results, expressed in terms of 0.1 *N* solution, are given in Table III.

Table III. Comparison of Benzoyl Auramine G and Methyl Red as Indicators in Presence of Ammonium Chloride

(The equivalence of the solutions was determined with bromothymol blue. 0.1 *N* solutions used in all cases.)

HCl Taken	NH_4Cl Added	NaOH Required to Obtain End Point	Indicator	Ratio of NaOH to HCl
Cc.	*Cc.*	*Cc.*		
50.00	None	50.00	Bromothymol blue	1.000
50.00	10	49.64	Benzoyl auramine G	0.993
50.00	40	49.67	Benzoyl auramine G	0.993
50.00	10	49.46	Methyl red	0.989
50.00	40	49.47	Methyl red	0.989

The ratio of the quantity of sodium hydroxide to that of hydrochloric acid required, in the presence of concentrations of ammonium chloride corresponding to those of the Kjeldahl titration, is closer to unity with benzoyl auramine G than with methyl red.

The indicator was tested under the actual conditions of routine macro-Kjeldahl titrations, in the determination of nitrogen in hide powder and gluten flour, and proved as satisfactory as methyl red. Artificial illumination was used. It was also tested in micro-Kjeldahl determinations and was found to meet the more exacting requirements of this method slightly better than methyl red.

Summary

A new indicator, benzoyl auramine G, is suggested for use in Kjeldahl titrations. Benzoyl auramine G changes from intense violet at pH 5.0 to pale yellow at pH 5.6. Other properties of the indicator are described, and a detailed method of preparation is given.

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Correction. In the article on "Baumé-Purity-Moisture Tables for Corn Sirup" [Ind. Eng. Chem., Anal. Ed., **7**, 41 (1935)], the first sentence on page 42 under the heading "Methods of Analysis" should read: "The moisture values given in Table I were made according to the A. O. A. C. method."

W. R. Fetzer

Identification of Certain Solvents by the Xanthate Reaction

Application to Alcohols

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WITHIN the past decade the application of chemical research to industrial problems has made available in quantity organic solvents which previously had been considered only as museum specimens or laboratory curiosities (*18, 25*). This development has been due chiefly to the investigation and utilization of products obtainable from petroleum and natural gas, although new synthetic and fermentation processes have played an important part.

The glycol ethers (cellosolves and carbitols) are comparatively recent additions to the increasing list of organic compounds which are of considerable technical importance. The identification and characterization of these forms is very difficult indeed if the conventional methods of qualitative organic procedure are followed.

This paper presents the results of an investigation which has led to the development of a satisfactory procedure for the identification of certain types of solvents.

PREVIOUS WORK

Although the monoalkyl ethers of ethylene and diethylene glycol have been available commercially during the past decade, no fundamental data exist in the literature for their qualitative identification by the usual scheme of organic analysis. However, Palomoa (*24*) and Conn, Collett, and Lazzell (*5*) prepared a series of aromatic esters of the monoalkyl ethers of ethylene glycol and diethylene glycol—the benzoyl and *p*-nitrobenzoyl derivatives—and found these esters to be liquids of high boiling point.

Zeise (*36*) was the first to report the formation of xanthic acid and its salts. Although Zeise reported many of the characteristic reactions of that substance of which we now have knowledge, it did not seem to have occurred to him that it could be extended to alcohols other than ethyl alcohol and it is only within comparatively recent times that it has been shown how extensive and characteristic xanthate formation is for the hydroxyl function. As a reaction leading to the formation of identifying derivatives, the xanthate reaction with but few exceptions has received but little attention. Bamberger (*2, 3*) studied and characterized the tetrahydronaphthols by this reaction. Tschugaeff (*31*) applied the xanthogenic reaction for the preparation of both characteristic derivatives of the terpene series and unsaturated hydrocarbons (Tschugaeff reaction), and further suggested its use for the differentiation of primary, secondary, and tertiary alcohols based on the stability of the xanthogenic acid esters on distillation (*10, 31*).

Probably the greatest single analytical application of the xanthogenic reaction is in the detection and quantitative estimation of carbon bisulfide. This is detected by absorption in alcoholic potassium hydroxide, which is then decomposed by making acid and adding copper sulfate. A golden yellow precipitate or coloration of cuprous xanthate forms, the test being sensitive to 1 part in 90,000 (*9, 32*).

For the quantitative determination of carbon bisulfide absorption in alcoholic potassium hydroxide, as before, is the first step. Variations from this point are based upon the manner in which the resulting potassium ethyl xanthate is estimated. Zeise (*35*) made ultimate analyses for the separate constituents. Hallet and Ryder (*12*) determined the xanthate by converting to the copper derivative, igniting, taking up the ash in nitric acid, and determining the copper electrolytically. Nickels (*23*) weighed the cuprous xanthate directly and was probably the first to weigh the potassium xanthate as such. Johnson (*17*) ignited the cuprous xanthate and weighed as cupric oxide. Macagno (*19*) and Hehner and Carpenter (*14*) titrated the cold aqueous solution of the xanthate, slightly acidified with acetic acid, with 0.1 *N* copper sulfate solution, determining the end point with potassium ferrocyanide. Selivounof (*27*) titrated the neutral solution of the xanthate with very dilute copper sulfate solution using guaiacol as indicator, extreme accuracy being claimed. Harding and Doran (*13*) precipitated the cuprous xanthate with an excess of copper acetate and determined the excess, after filtration, iodometrically. Calcott, English, and Downing (*4*) precipitated the cuprous xanthate, filtered, decomposed the residue with nitric acid, and determined the copper iodometrically. Matuszak (*21*) decomposed the cuprous xanthate with bromine water and estimated the copper iodometrically.

Holmberg (*16*) and Hirschkind (*15*) added excess of standard acid to the aqueous solution of the xanthate, allowed it to stand for 10 minutes, and back-titrated with standard alkali (barium hydroxide) using either phenolphthalein or methyl red as indicators. Stavorinus (*28*) and Weiss (*33*) oxidized the xanthate solution with hydrogen peroxide and determined the resulting sulfate either gravimetrically or volumetrically in the usual manner. Tarugi and Sorbini (*29*) added the unknown xanthate solution to a standard solution of arsenic trioxide, extracted the arsenic xanthate with an organic solvent, and titrated the aqueous layer containing excess of arsenic with iodine.

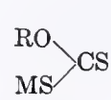
The direct titration of xanthate solutions with iodine is based upon the following reaction:

$$I_2 + 2C_2H_5O.CS.S^- = 2I^- + (C_2H_5O.CS.S)_2$$

and seems to have been first proposed by Delachanal and Mermet (*7*), although the action of iodine on xanthates was studied as early as 1845 by Zeise (*34*). The reaction is of quantitative accuracy and has the important advantage of being very easily and quickly carried out. In this respect it stands in marked contrast to the methods enumerated above as the operations of precipitation, filtering, washing, etc., are eliminated. The quantitative aspects of the reaction have been studied and reported by Gastine (*11*), Rupp and Krauss (*26*), Andre (*1*), Cundal (*6*), and Matuszak (*20*), the latter critically discussing the previous work on the subject.

PRINCIPLE OF ANALYTICAL SCHEME

From an examination of the literature of the xanthate reaction it is evident that numerous methods exist for the quantitative estimation of the alkali xanthates. In spite of the large amount of work which has been done upon that problem with respect to the determination of carbon bisulfide, no one has ever suggested its systematic extension to the identification of alcohols. The general formula of an alkali xanthate is:



where

R = an alkyl residue
M = an alkali metal

If we apply one of the methods used for the quantitative estimation of a xanthate, it is evident that the amount of

standardized reagent, whether it be copper solution, acid, or iodine solution, will depend upon the molecular weight of R. Hence it is possible to assign to each alcohol an "alkali xanthate reagent number" which will sharply characterize the alcohol.

A review of the quantitative methods cited for the estimation of the xanthate used indicated that the direct titration with iodine was the simplest, quickest, and quite accurate.

Materials and Reagents

Purification of Alcohols. All of the alcohols and monoalkyl ethers of ethylene and diethylene glycol studied in this paper were purified by careful fractionation with forced reflux and only the purest fraction of each substance was taken. Table I presents the physical data obtained for the monoalkyl ethers of ethylene and diethylene glycol obtained by purification of commercial samples of the cellosolves and carbitols obtained through the courtesy of the Carbide and Carbon Chemicals Corporation.

Table I. Physical Properties

Solvent	Boiling Point, ° C.	Specific Gravity $\frac{20}{20}$	Refractive Index 20° C.
	ETHYLENE GLYCOL		
Monoethyl ether	134.7–135	0.9305	1.4077
Monomethyl ether	124.4	0.9605	1.4017
Monobutyl ether	169.3–169.5	0.9027	1.4190
	DIETHYLENE GLYCOL		
Monoethyl ether	194–195	1.0397	1.4300
Monobutyl ether	228.5–230.0	0.9650	1.4321

Reagents. The potassium hydroxide and carbon bisulfide were of c. p. reagent grade. The ethyl alcohol and acetone used for purifications were c. p. absolute. The diethyl ether used was of ordinary grade. This was allowed to stand over calcium chloride for several days, and then stored over sodium, and was filtered before use.

Standard Iodine Solution. This was prepared as outlined by Treadwell and Hall (*30*) and standardized by methods indicated in that text. One cubic centimeter of the standard iodine solution employed contained 0.00952 gram of iodine.

Starch Solution. This was prepared fresh before use by dissolving 0.5 gram of soluble starch in 100 cc. of boiling water.

Experimental Procedure

Preparation and Purification of Alkali Xanthates. To 1.2 molar proportion of the purified alcohol was added 1.0 molar proportion of pulverized potassium hydroxide, and the mixture heated with stirring until the alkali dissolved. To this an equal volume of dry ether was added after cooling, and then a 1.5 molar proportion of carbon disulfide was gradually added in small portions with vigorous stirring. The yellow precipitate of the xanthate formed immediately. After the addition of carbon disulfide, two additional volumes of ether were added, and the product was filtered off on a Büchner funnel, pressed, and washed with dry ether. The product was removed from the funnel, washed again with dry ether by agitation, and refiltered.

In order to purify, the product was dissolved in the smallest quantity of hot ethyl alcohol or acetone, filtered, cooled in an ice bath, and dry ether added to complete precipitation. The recrystallized product was filtered off on a Büchner funnel, pressed, and washed with dry ether. In all cases the above procedure was repeated to give the final purified product used in the subsequent work. The final product was then dried in a vacuum desiccator for several hours or, when convenient, overnight.

Iodometric Titration of the Alkali Xanthates. From 0.15 to 0.25 gram of the purified xanthate was dissolved in 200 cc. of water. After the addition of 4 cc. of freshly prepared starch solution, it was titrated directly with the standardized iodine solution to a distinct blue end point which should be permanent for at least 5 to 10 minutes. The addition of iodine was accompanied by vigorous agitation. As the iodine is added a whitish emulsion appears, consisting of the resulting "dixanthogen."

The iodine equivalent of the xanthate was calculated from the experimental data as follows:

$$I_x = \frac{C \times I}{G}$$

where

I_x = iodine equivalent of the xanthate expressed in milligrams of iodine per gram of xanthate
C = volume in cc. of iodine solution required
I = value of iodine solution expressed in mg. of iodine per cc.
G = weight of alkali xanthate taken expressed in grams

Calculation of Theoretical Iodine Equivalent Values. The theoretical iodine equivalent values for the alkali xanthates are based upon the reaction equation:

$$2KX + I_2 = 2KI + X_2$$
$$\text{where } X = (RO.CS.S^-)$$

i. e., two moles of xanthate are equivalent to one mole of iodine.

Figure 1 summarizes in graphical form, with typical examples cited, the theoretical xanthate iodine equivalents of the alcohols studied in this report. The practical use of this curve is discussed below.

Determination of Melting Points. Melting points were determined with the apparatus and procedure described by Mulliken (*22*).

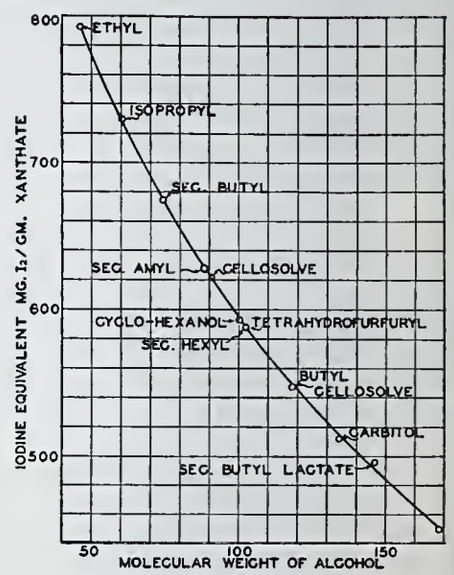


Figure 1

Experimental Results

The experimental data obtained in the manner outlined above are summarized in Table II.

Melting point determinations are similarly summarized in Table II. In general the majority of the melting points lie above 200° C. and for many of the alcohols are quite close together. Attention is, however, directed to the characteristic melting points of the monoalkyl ethers of ethylene glycol (cellosolves) xanthates.

Unsaturated Alcohols. Furfuryl and allyl alcohols were chosen as representative of this class. The potassium xanthates were prepared and purified in the manner described and titrated with iodine. Allyl potassium xanthate behaved normally and gave experimental values in excellent agreement with theory. Furfuryl potassium xanthate gave high values due to addition of iodine to the double bonds.

Tertiary Alcohols. Experimental data upon the potassium xanthates derived from tertiary alcohols (butyl and amyl) confirmed the previous work of Dubsky (*8*) on the instability of these products. It was not possible to obtain any definite xanthate iodine equivalent values, data in all experiments being 30 to 40 per cent high and with no permanent end point. It was found that aqueous solutions of the tertiary xanthates quickly develop an odor of hydrogen

sulfide, easily confirmable by moist lead acetate paper. The probable reaction is

$$(R)_3CO.CS.SK + HOH = (R)_3C.OH + KHS + COS$$
$$COS + HOH = CO_2 + H_2S$$

In all probability the decomposition is further catalyzed by the products of decomposition, since hydrogen ions are produced. Xanthates derived from primary and secondary alcohols are stable in aqueous solution, but decompose slightly with evolution of hydrogen sulfide on prolonged boiling. The tertiary xanthates decompose rapidly in boiling aqueous solution.

Monoalkyl Ethers of Glycols. The monoalkyl ethers of ethylene glycol (cellosolves) yielded with no difficulty nice crystalline potassium xanthates of definite melting points, which gave iodine values agreeing closely with the calculated values (Table II).

Table II. Identification of Alcohols as Xanthates

Type	RO.CS.SK R	Iodine Equivalent[a] Expt.	Calcd.	Melting Point Cor.
		Mg./g.	*Mg./g.*	° *C.*
Primary	Methyl	874	869	Darkens at 195–215
	Ethyl	797	793	215.3
	Propyl	726.5	729	205.7
	Butyl	676.5	675	223.9
	Amyl	625	628	225
	Tetrahydrofurfuryl	590	587.5	213.2
Secondary	Propyl	721	729	Darkens at 236
	Butyl	671.5	675	244.1
	Amyl	633	628	211.7
	Hexyl	592	587.5	Darkens at 199
	Cyclohexanol	589	593	Darkens at 242
Cellosolves	Cellosolve	620.5	622	185.7
	Methyl	667	668	202.5
	Butyl	544	547	167.9
Carbitols	Carbitol	516	512	...
	Butyl	425	460	...
Unsaturated	Furfuryl	...	599	154.4
	Allyl	740.5	738	Darkens at 178

[a] Mg. of iodine per gram of xanthate.

Some difficulty was experienced with the carbitols (monoalkyl ethers of diethylene glycol) in a manner which sharply distinguished them from the cellosolves. Preparation of the corresponding potassium xanthates in the usual manner yielded heavy red oils instead of the customary bulky yellow precipitates. The reddish oils are insoluble in ether and soluble in water. On the addition of copper salts to the aqueous solution, heavy precipitates of the brilliant golden yellow cuprous derivatives were thrown down. Like the solid alkali xanthates, the reddish oils were soluble in acetone and benzene, and were reprecipitated by addition of ether. These oils were then drawn off, washed several times with ether by agitation, then placed in wide crystallizing dishes and allowed to dry in a vacuum desiccator for several days. Carbitol (monoethyl ether of diethylene glycol) yielded an orange-colored pasty solid (melting point, 127° C.), while butyl carbitol (mono-*n*-butyl ether) gave a thick reddish jelly-like solid. Both were titrated in the usual manner with iodine. The results are indicated in Table II. Carbitol shows good agreement with the calculated value, while butyl carbitol, although low, is only 7.6 per cent from the theoretical value.

Discussion

The method outlined above presents a relatively simple means for the identification of alcohols with reagents which are inexpensive and found in every laboratory. The procedure is relatively simple, rapid, and requires no unusual experience. Further, as may be noted from an examination of Figure 1, the determination of the xanthate iodine equivalent also leads to the simultaneous determination of the molecular weight of the unknown alcohol. The usual characterizing derivatives for this group, the 3,5-dinitrobenzoates and the phenyl urethanes, give no further information than a melting point, a physical constant which is extremely sensitive to even traces of impurities. An examination of a table of melting points of a series of 3,5-dinitrobenzoates further reveals melting points too low for convenient measurement, and in some cases the derivatives of alcohols boiling at substantially the same temperature have melting points which are so close together that definite characterization by this derivative alone is impossible.

Isomeric alcohols yield the same xanthate iodine equivalent. Identification is, however, possible because of differences in physical constants and melting points of the individual xanthates.

While pure and anhydrous alcohols were used in establishing the reliability of the method, in actual practice this need not be the case. The analyst is frequently in possession of sufficient facts concerning his unknown, so that extensive isolation, purification, and determination of physical constants are unnecessary. The alcohol need not be anhydrous, as the alkali xanthates form in the presence of water. The method may be applied directly to a solvent mixture, provided only one alcohol is present. The curve of Figure 1 is particularly helpful where only a boiling point determination is available.

A method for the direct identification of the alkoxy group in esters, based upon the xanthate reaction, has been developed and will be presented in a separate report.

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Syringe Pipets

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In several cases the author has been confronted in the laboratory with the problem of measuring off small volumes of fluids which must not come in contact with air—e. g., barium hydroxide for microtitration—and this led to an attempt to use the record syringes well known in medical technic. The somewhat surprising result of these attempts was that a syringe with the piston working between two fixed stops was not only much quicker than a pipet of the same volume, but also definitely more accurate. On the basis of this observation several types of measuring syringes or syringe pipets have been constructed (*1*).

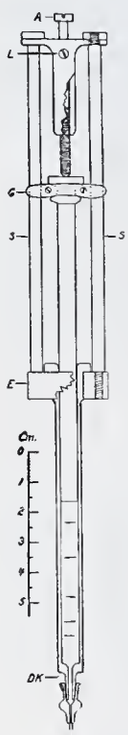

Figure 1

The first step was to discard the metal piston which limits the applicability to relatively few solutions. An all-glass syringe of 2-cc. capacity was found suitable and was mounted as shown in Figure 1 with an adjustable stop and a cannula which is generally of stainless steel, but can be made of glass or other suitable material. This syringe will measure any desired volume between 0.1 and 1.5 ml., and an accuracy of ±0.0001 ml. is easily obtained. With the very best syringes and the utmost care the error can be reduced to ±0.00002 ml. With pipets of similar size it is very difficult to obtain an accuracy of 0.001 ml. and usually the error will be even larger.

The correction for temperature is an important consideration when the accuracy is of the order of 0.0001 ml. Within the temperature interval from 15° to 25° C. the temperature correction of these syringes is negligible (less than 0.0001 ml.), because the steel rods carrying the adjustable stop were selected to compensate the change in the glass parts.

Somewhat larger syringe pipets being desirable for several purposes, while a somewhat lower standard of precision is in most cases sufficient, a syringe pipet of simpler design was constructed as shown in Figure 2. This is relatively shorter and has no separate cannula, but ends in a capillary tube which can be drawn out as desired and is fairly easy to replace. Syringe pipets are made in 10-, 5-, 2-, and 1-ml. sizes and by means of the screw at the top can be adjusted to deliver any volume between 10 and 0.1 ml.

The adjustment and calibration of a syringe pipet are performed by delivering and weighing distilled water, and it has been found convenient to use one weighing bottle in each pan of the balance into which the volume is delivered alternately. On a modern damped balance one has then only to move a single weight back and forth.

The 10-ml. syringe is exceptionally accurate, while the 1-ml. syringe is of average accuracy. The pistons fit so snugly that the increase in resistance produced by pressing the cylinder between two fingers is generally very pronounced. This makes the fitting of the frame for the top screw difficult, but on the other hand it makes the accuracy of the measurement quite independent of the viscosity of the fluid.

A definite source of error is due to the fact that the lower surface of the piston is not as a rule absolutely perpendicular to the axis. If the piston is turned when in the bottom position, a meniscus in the cannula is seen to move slightly forward and backward. In accurate measurements the piston therefore must not be turned, the square top of the piston being kept parallel to the square top of the cylinder.

The temperature sensitivity of these syringes is greater than that of the precision syringes, but still so small that it can in most cases be disregarded. For instance, a syringe delivering 5.000 ml. at 20° C. was reduced to 4.996 ml. at 4° C., while another was reduced from 10.000 to 9.994 ml.

Table I. Calibrations

	Syringe A		Syringe B	
	Water delivered	Difference from mean	Water delivered	Difference from mean
	Grams		*Grams*	
	9.9680	−0.0005	0.9966	+0.0001
	9.9690	+0.0005	0.9967	+0.0002
	9.9684	−0.0001	0.9965	.....
	9.9683	−0.0002	0.9966	+0.0001
	9.9683	−0.0002	0.9962	−0.0003
	9.9689	+0.0004	0.9963	−0.0002
Mean	9.9685		0.9964	−0.0001
			Mean 0.9965	

When the same syringe has to be used for different solutions in succession, the dead space from the tip of the cannula to the bottom position of the piston is a drawback. Most of the fluid in it can be removed as a spray of fine drops by rapidly moving the piston up and down. After using a syringe for 20 per cent hydrochloric acid, the author has emptied it in this way and washed twice with about one-third volume of water which was removed from the dead space in the same manner; he has then taken in one-third volume of water to fill up the dead space and thereupon used the syringe for water which was shown by the addition of an indicator to have a pH of 5.5. The acid left in the syringe raised the pH to about 5. The total time for the washing was just under 1 minute.

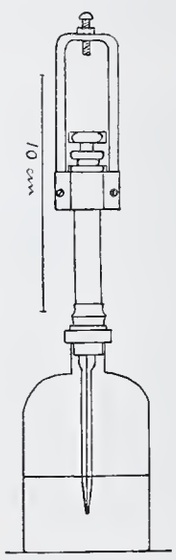

Figure 2

When a fluid is sucked up too rapidly, so that a considerable force must be used to overcome the resistance in the cannula, bubbles of air are likely to become liberated in the syringe. Small bubbles which remain in the syringe do not interfere with the accuracy as measured by the delivery.

It has been pointed out as a possible source of error in measuring solutions that water will evaporate from the upper part of the piston when this becomes exposed in filling the syringe and the concentration of the content is thereby gradually raised. It is true, of course, that a little fluid is transported along the piston and becomes concentrated even to dryness in the top of the cylinder. When a syringe has been used for some days or weeks, a noticeable amount of salt may accumulate in this place. Fluid is carried, however, from within outward only, by reason of the capillarity between the piston and syringe. When the piston is pushed down, even after having become completely dry by evaporation, fresh fluid is sucked in by capillarity from below and no mixture takes place through a capillary space 1.5 to 3 cm. in length. Even when the space between the collar of the syringe and the piston is filled with fluid, admixture of this fluid with that measured off below the piston is negligibly small, as shown by the following experiment:

The space between the collar and the piston in a 2-ml. syringe was filled with 20 per cent hydrochloric acid. The syringe was filled and emptied 20 times in 2.5 minutes from 10 ml. of distilled water in a basin. An indicator would show the addition of 1 volume of the acid in 100,000 volumes of water. The acidification observed was 1 in 50,000. A similar experiment with a 10-ml. syringe filled 20 times in 5 minutes from 20 ml. showed no detectable acidification.

Syringes which are not used constantly should be washed out with water to prevent the piston's sticking fast. The author has found it possible, however, in such cases to loosen it by treatment with hot water.

It is possible with syringe pipets to work several times more rapidly and at the same time with much greater precision than with pipets of the same volume, but the higher price will prevent their being generally used.[1] They have been found especially suitable for the following purposes:

Serial measurements of the same fluid, for which purpose it is often advantageous that the syringe can be easily arranged to deliver any desired volume.

Measurement of viscous fluids.

Delivery of fluids which must not come into contact with air.

All measurements in which more precision is desired than can be obtained by means of ordinary pipets.

(The author has made many determinations of specific gravity of solutions by measuring with a syringe and weighing as described for the calibration, and has used syringes in combination with a small buret for precision titrations.)

In many cases chemical reactions can with advantage be arranged to take place in syringes, especially when it is essential to exclude atmospheric air.

[1] The Laboratory of Zoöphysiology is prepared to supply precision syringes mounted with an ordinary stainless-steel cannula at a price of 25 Danish kroner; glass cannula, 2 Danish kroner; and cannula made entirely of stainless steel, 12 Danish kroner. The prices of the ordinary syringe pipets here described are: for 1 and 2 ml., 10 Danish kroner; 5 ml., 12 Danish kroner; 10 ml., 15 Danish kroner, at the laboratory. The 10-ml. pipet is provided with an extra movable stop on one of the guide rods for preparing definite mixtures.

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Precise Determination of Oxygen in Water by Syringe Pipets

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Oxygen titration in water is carried out according to Winkler by adding a known small amount of alkali containing potassium iodide (reagent I) and then a corresponding volume of manganous chloride (reagent II). Manganous hydroxide is thereby formed as a voluminous precipitate which absorbs the free oxygen. After acidification with hydrochloric acid, iodine equivalent to the oxygen is liberated and is titrated with thiosulfate. It is customary to utilize water samples of 100 ml. or more, measured in glass-stoppered bottles. For years in the author's laboratory a micro-Winkler method has been used, in 7- to 15-ml. bottles titrating 5-ml. samples from a 2-ml. buret with 0.005 *N* thiosulfate. A micromethod described by van Dam (*3*) utilizes a 1-ml. syringe and a Rehberg microburet.

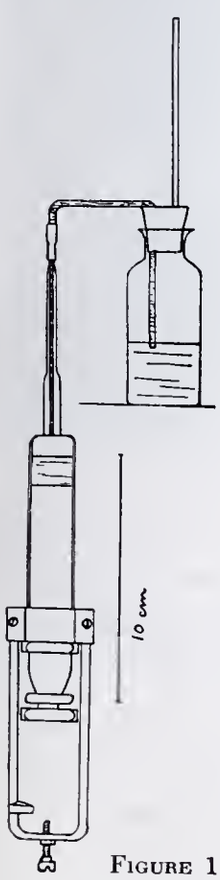

Figure 1

In oxygen determinations as hitherto performed there are two main sources of error which should be eliminated. One is the diffusion of oxygen that takes place whenever the sample is not in equilibrium with the atmosphere, and the other is the uncertainty of the correction for oxygen dissolved in the reagents. These sources of error are completely eliminated in the procedure described below.

The water sample is collected and the reaction carried out in a 10-ml. syringe pipet, slightly modified as shown in Figure 1, by arranging a fixed stop on one of the guide rods. This stop is placed so as to correspond as nearly as possible to 10.00 ml. and the screw stop is set at a definite distance above, corresponding to about 0.1 ml. more. For a determination, the dead space of the syringe is first washed out and filled with reagent I, care being taken that no air bubbles remain in the syringe or cannula. As much water as possible is removed from the syringe before taking in the reagent, but since this cannot be done completely the reagent in the bottle becomes slowly diluted. The tube through which the reagent is taken in therefore reaches only halfway down the bottle and the rest of the content is discarded. As pointed out by Yoder and Dresher (*4*), rubber may give off sulfur and a ground joint in the top of the bottle will be preferable to the rubber stopper shown.

The sample of water is drawn in slowly until the top of the piston comes against the fixed stop, and finally the piston is turned free of the stop and reagent II drawn in quickly. The tip of the cannula is wiped off between each intake and is finally closed by means of a small piece of rubber tubing with a glass stopper. It is convenient to put this on filled with water. The syringe is well shaken and placed with the tip upward, so that the precipitate collects on the piston. The syringe should be left in this position for 0.5 hour to allow the precipitate to settle. If left longer a firm clot of precipitate may form in the cannula, which may have to be pushed down by means of a fine wire before the syringe can be emptied. It is now possible to drive out almost all the fluid without losing any of the precipitate, to take hydrochloric acid into the syringe, and titrate in a small volume of fluid, but the manganous hydroxide is not sufficiently insoluble to make this procedure advisable (except perhaps when the amount of oxygen is very small). It is therefore necessary to titrate on the total volume of fluid. A suitable quantity of hydrochloric acid (0.4 ml., 20 per cent) is measured off into a flat-bottomed test tube of 30 × 100 mm. (as used for Hagedorn blood-sugar determination). Some fluid from the syringe is driven out into this and taken back again, so that the main reaction takes place in the syringe.

The content of the syringe can be titrated from a 2-ml. buret with 0.01 *N* thiosulfate and, in comparative determinations an accuracy of 0.005 ml., corresponding to about 0.04 ml. of oxygen per liter, is easily obtained. The author has endeavored to obtain a definite improvement in the accuracy of this determination and has come across several sources of error which can be overcome by a suitable technic.

Necessary Precautions

1. Since it is difficult to add less than 0.003 ml. from a 2-ml. buret, the author has used a weaker solution of thiosulfate made up to 0.003572 N so that 1 ml. corresponds to 0.02000 ml. of oxygen (0°, 760 mm.). When 0.1 gram of cyanide of mercury per liter is added to this solution, it is perfectly stable and only has to be guarded against evaporation. Titrating with this solution the result when multiplied by 2 gives the milliliters of oxygen per liter.

2. When the iodine liberated in a sample corresponds to more than 0.5 ml. of this thiosulfate, a loss of iodine, which may reach 1 per cent, will take place by evaporation. This is avoided, however, when the titration is carried out by a combination of syringe pipets and a 2-ml. buret, which will, moreover, increase materially the rapidity and accuracy of the determination.

In all precision determinations it is necessary to have a fair approximation of the result beforehand. The thiosulfate solution should be ready in the buret and also in a three-necked Woulff bottle mounted with 3 syringes delivering 2.000, 1.000, and 0.500 ml., respectively. A suitable quantity of thiosulfate is measured off by means of 1 or more of these syringes, and starch (3 drops) is added before the syringe containing the free iodine is emptied; the mixture can now be titrated from the buret with not more than 0.5 ml. until the blue color disappears. The syringe is washed out at this stage by filling and emptying it once from the titrated mixture and the titration is finished. The exact point of disappearance of the color is obtained by means of a comparison vessel. Performed in this way, a series of titrations of the same fluid will agree within ±0.005 ml. or 0.01 ml. of oxygen per liter, 0.01 ml. of oxygen per liter corresponding to 0.0001 ml. of oxygen in the syringe or the oxygen in an air bubble 1 mm. in diameter. Usually the results are even better. It is evident therefore that even small bubbles of air make the accuracy illusory.

3. As shown by Yoder and Dresher (*4*), the quality of the starch is an important consideration. Certain starches have a greater affinity for iodine than others, as measured by the quantity necessary to produce a just visible blue color. As is well known, this affinity is a function of temperature. The ideal starch should show the highest possible affinity, which should be practically independent of temperature within the range usually met in the laboratory. The starch as used by the author is prepared according to Hagedorn by dissolving 1 gram of the starch by heating in 100 ml. of saturated sodium chloride, giving a solution which is not attacked by bacteria and is perfectly stable. Three drops (0.12 to 0.15 ml.) of this solution are added to 10 to 15 ml. of fluid.

The starch is tested as follows:

To 10 ml. of water with 0.1 to 0.2 ml. of reagent I, 0.3 ml. of 20 per cent hydrochloric acid, and 3 drops of the starch, add from a 2-ml. buret 0.0002 N iodate until the color can be just distinguished from pure water. This test is performed at different temperatures, each time on a fresh sample because the blue color when already present is scarcely changed by temperature inside the range from 16° to 30° C. which is of practical importance.

The following starches were tested:

	Iodate Added		
	16°	22°	30°
	Ml.	*Ml.*	*Ml.*
1. Merck's C. P. soluble in sodium chloride	0.07	0.085	0.10
2. Starch of low solubility stabilized with mercuric iodide	0.10	0.125	0.155
3. Soluble starch in sodium chloride	0.08	0.135	0.18

Merck's soluble starch shows the highest sensitivity and the lowest temperature coefficient. The temperature coefficient of No. 2 is definitely lower than of No. 3.

The result is calculated as a correction which must be added to the oxygen directly determined by the titration. The correction is proportional to the total titration volume, which can be taken as 10.5 ml. plus the volume of thiosulfate used. For Merck's soluble starch this correction works out as 0.0010 ml. of oxygen per liter for each milliliter of total volume at 16°, 0.0012 at 22°, and 0.0014 at 30° C. This correction can also be calculated from a series of titrations of known dilutions of iodate measured off by means of a syringe pipet. Values for starch No. 3 at 22° are given in Table I.

Table I. Titration Values for Starch No. 3

Iodate	Titration	Corrected	Calculated	Variation
N	*Ml.*	*Ml.*	*Ml.*	
0.00200	5.588	5.671	5.675	+ 4
0.00120	3.333	3.404	3.405	+ 1
0.00100	2.772	2.840	2.837	− 3
0.00080	2.206	2.272	2.270	− 2
0.00040	1.074	1.134	1.135	+ 1
0.00020	0.508	0.565	0.568	+ 3
0.00010	0.229	0.284	0.284	0
0.00008	0.175	0.230	0.227	− 3
0.00004	0.069	0.123	0.114	− 9
0.00002	0.026	0.080	0.057	−23

The results between 0.002 and 0.00008 N correspond to a correction figure of 0.0104 ml. of oxygen per liter per milliliter of titration volume. The figure is much higher than the value deduced above and was found to be valid only for oxygen concentrations from 0.4 ml. of oxygen per liter upwards. For starch No. 1 a corresponding test showed substantial agreement with the simple color test, giving at 22° a correction figure of 0.0014.

4. During the titration direct sunlight should be avoided, because it may accelerate the liberation of iodine from the iodide present to such an extent as to interfere with the titration. Most constant results have been obtained in artificial light.

5. In the oxygen determination proper allowance must be made for the oxygen present in the reagents. The quantity of reagent depends upon the dead space of the syringe and may vary somewhat from one syringe to another. The volume is determined by titration. The dead space is filled with some suitable normal solution washed out with distilled water, and titrated. In his syringes the author has found volumes between 0.18 and 0.25 ml. The proportion between reagent I and II can be varied within wide limits. The author prefers to set the top screw so as to make the quantity of II just half that of I, which is amply sufficient for any ordinary quantity of dissolved oxygen. The setting is easily performed by connecting the syringe filled with water with a 1-ml. pipet divided in 0.01 and observing the movement of the meniscus when the piston is moved from stop to top screw.

The oxygen present in the reagents was measured in one series of determinations by filling up the syringe with oxygen-free water and titrating this. Absolutely oxygen-free water is difficult to prepare and it is simpler to mix the concentrated reagents in the right proportions directly in a 2-ml. syringe pipet. After 0.5 hour the content is poured into 10 ml. of suitably diluted hydrochloric acid and titrated as usual. The two methods have given identical results.

The reagents as usually employed are:

I. 33 grams of sodium hydroxide and 10 grams of potassium iodide made up with water to 100 ml.

II. 40 grams of manganous chloride made up with water to 100 ml.

When I and II are mixed in the proportion 2 to 1 and saturated with atmospheric air at 20° to 22° C., the solution will contain 3.4 ml. of oxygen per liter as against 6.4 in pure water.

6. The acid added to liberate the iodine must be present in fairly large excess to secure complete solution of the precipitate within the syringe. A large excess accelerates the secondary reaction of liberating iodine from the iodide, but when strong light is avoided, this reaction is too slow to interfere. The author has tried only hydrochloric acid and has chosen

20 per cent as the most convenient concentration; 0.25 ml. is theoretically sufficient when the volume of the reagents is 0.3 ml., but 0.4 cc. is taken when the reagent volume is less than 0.3, and 0.5 ml. when it is above.

7. Results obtained on the same water by the author have varied by ±0.007 ml. of oxygen per liter. The accuracy is sufficient to warrant calibration and correction of the 2-ml. buret employed, as errors on these burets up to 0.01 ml. are not uncommon. A comparison of the absolute values for distilled water at different temperatures with Fox's (*1*) tables revealed a systematic discrepancy of 1 per cent which has to be added to the titration results. A similar discrepancy has been observed before (*2*), but an explanation has not, so far, been found.

Conclusions

The method described was worked out mainly for biological purposes, but should also be useful industrially for the determination of oxygen in deaërated water. A serious source of error in the Winkler titration of water with a very low oxygen content is the rapid absorption of air from the atmosphere. This error is counteracted, but cannot be abolished, by taking very large samples. In the syringe method here described any possibility of contamination with air is excluded. When the amount of oxygen is below 0.5 ml. per liter there is no danger of loss of iodine, the buret only is required for the titrations, and the corrections for final volume and for oxygen in the reagents can be combined.

Summary

By the use of 10-ml. syringe pipets for the Winkler determination of oxygen in water, contamination with air from the atmosphere can be completely avoided. The accuracy can be increased at least to ±0.007 ml. of oxygen per liter, by avoiding loss of iodine and by corrections for the final concentration of iodine and for oxygen in the reagents.

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Received September 18, 1934.

Fluorescence of Gaseous Acetone as a Test for Traces of Oxygen

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In a recent investigation by Damon and Daniels (*1*) it was noted that the photolysis of pure acetone vapor was accompanied by a relatively intense green fluorescence. However, when even a trace of oxygen was present in the reaction cell, the fluorescence was a faint blue instead of green. It was also found that a sharp change in color from blue to green took place when the irradiation was continued for a period of time, roughly dependent upon the amount of oxygen present in the cell. This change in fluorescence suggests the possibility of its use as a sensitive semi-quantitative test for traces of oxygen.

A method for the detection of traces of oxygen in samples of various gases should have a wide range of application, provided the gases with which the oxygen is mixed have no effect on the fluorescence of the acetone. Qualitative tests (*1*) show that nitrogen, hydrogen, carbon monoxide, carbon dioxide, chlorine, ethylene, methane, ethane, ethyl ether, and water have no effect on the fluorescence of pure acetone vapor. The time for the color change from blue to green was not materially changed by the addition of the above-mentioned gases.

Apparatus

The apparatus is relatively simple and inexpensive. Figure 1 shows the essential materials for this work. Auxiliary apparatus for the purification, storage, and transfer of gases may be required. A capillary quartz mercury vapor lamp (*2*), *A*, is the most satisfactory source of ultraviolet light, but a commercial lamp was found to give sufficient intensity for the test, and has the advantage of a more uniform intensity over a long period of time. A Corning Red Purple Corex No. 986 light filter, *B*, satisfactorily cuts out the visible light in the mercury arc. *C* is a 6-cm. quartz focusing lens (f = 10 cm.). The reaction cell, *D*, is made from a round-bottomed Pyrex flask. Pyrex glass cuts out all radiation of a wave length less than 3000 Å., but the 3130 Å. line of the mercury arc is transmitted with sufficient intensity for this test. In order to observe the fluorescence change, the reaction cell must be either in a dark room or in some type of enclosure which can be made relatively dark.

Maximum Sensitivity of Test

The maximum sensitivity of the fluorescence test for oxygen is determined by introducing known quantities of air into a cell containing pure acetone vapor.

Air is sealed into a thin glass capillary tube, *I*, of known volume. The side container, *H*, is then sealed onto the main cell at *G*. Liquid acetone is placed in *E* and the entire system evacuated until most of the liquid acetone is evaporated and all air removed.

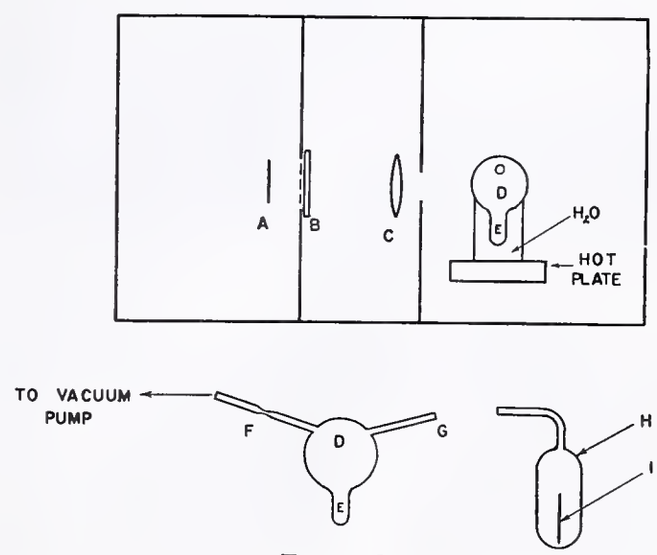

Figure 1

The cell is sealed off at *F* and placed in the water bath, where the pressure of the acetone vapor is raised to and kept at approximately one atmosphere. The appearance of a green fluorescence on irradiation proves that the cell is free from all oxygen except that in the capillary. The oxygen is introduced by removing the cell from the water bath and breaking capillary *I* by striking it against the bottom of container *H*. The sensitivity of the test is then determined by the time of irradiation required for the reappearance of the green fluorescence.

Table I shows typical results using a capillary arc lamp. Variations in the intensity of the incident light and in the measurement of such small quantities of oxygen prevent the test from being rigidly quantitative, but the data show that the test is sensitive to approximately one micromole of oxygen.

Table I. Sensitivity of Fluorescence Test

Test No.	1	2	3	4
Volume of O_2 (S. T. P.), cc.	0.094	0.020	0.006	0.003
Time to green fluorescence, min.	12	5	2	<1
Partial pressure of O_2, mm.	0.031	0.07	0.02	0.01
Molecules $O_2 \times 10^{-17}$	25.4	5.7	1.6	0.8

Application of Method

The all-glass technic used to obtain the data of Table I is not readily applicable to the rapid semi-quantitative detection of oxygen. The detection of oxygen in commercial tank nitrogen illustrates the procedure for the calibration of the light source and the estimation of the amount of oxygen in an unknown sample of a gas.

The nitrogen was first analyzed for oxygen by the Hempel method, using a freshly prepared phosphorus pipet. The analysis of several samples showed the oxygen content to be less than the sensitivity of the method. This indicates that the amount of oxygen in the nitrogen is less than 0.2 per cent.

The apparatus was modified to facilitate the introduction of relatively large samples of nitrogen. Vacuum stopcocks were sealed onto the cell, *D*, at *F* and *G* (Figure 1). The nitrogen could then be introduced through *G* from a calibrated mercury gas pipet. Extreme care was taken to see that all connections and stopcocks were air-tight.

Table II. Relative Efficiencies of Alkaline Pyrogallol and Phosphorus in the Removal of Oxygen from Nitrogen

Test	Nitrogen Added	Nitrogen Passed Through	Time to Green Fluorescence	Average Time for 20 Cc.
	Cc.		*Min.*	*Min.*
1	22.0	Nothing	27	..
2	22.4	Nothing	30	..
3	22.8	Nothing	45	30.3
4	22.3	Alkaline pyrogallol	11	..
5	22.0	Alkaline pyrogallol	9	9.0
6	19.7	Phosphorus	6	..
7	18.3	Phosphorus	5	..
8	18.8	Phosphorus	7	6.3

Table II shows typical results obtained for tank nitrogen, nitrogen passed slowly through two 6-inch towers of freshly prepared alkaline pyrogallol, and nitrogen after standing in a phosphorus pipet. A capillary arc lamp was used in these tests, but a commercial lamp was shown to give similar results. The data show that even phosphorus will not remove all traces of oxygen from nitrogen. For semi-quantitative purposes it may be assumed that the amount of oxygen in a sample is directly proportional to the time required for the fluorescence change. In this case the phosphorus removed approximately 79 per cent of the oxygen from the tank nitrogen, while the pyrogallol removed approximately 70 per cent of the oxygen.

The estimation of the amount of oxygen in tank nitrogen was obtained indirectly from the data of Table II.

A 100-cc. gas buret was almost filled with nitrogen and all possible oxygen removed by phosphorus. To 99 cc. of this nitrogen was added 0.3 cc. of air. Tests were made alternately with samples of the air-nitrogen mixtures and with the regular tank nitrogen. The amount of foreign gas added was regulated until the time for the fluorescence change in a sample of the mixture was the same as for a sample of tank nitrogen. The amount of oxygen added to the air-nitrogen sample was assumed equal to the amount of oxygen which could have been removed by phosphorus from the sample of tank nitrogen. It was found that 20.7 cc. of the air-nitrogen mixture required the same time for the fluorescence change as 17 cc. of the tank nitrogen. On the basis that phosphorus removes 79 per cent of the oxygen from tank nitrogen, as calculated from the data of Table II, the nitrogen analyzed contained 0.0014 cc. of oxygen per cc. of nitrogen. This figure is equivalent to 0.14 per cent, which was too small to determine by the Hempel method. Nitrogen which has been passed over phosphorus still contains 0.03 per cent oxygen, while the alkaline pyrogallol left oxygen equivalent to 0.043 per cent.

Proposed Procedure

Use the apparatus of Figure 1 with vacuum stopcocks sealed onto the reaction cell at *F* and *G*. Introduce the gas to be tested through *G* from a calibrated mercury pipet. An immediate green fluorescence on irradiation proves that the gas sample contains less than one micromole of oxygen. If fluorescence is blue, determine the time required for the appearance of the green fluorescence. Calibrate the light source by determination of the amount of oxygen in tank nitrogen by the method described. Estimate the amount of oxygen in the unknown sample of gas by comparing the time for the fluorescence change with the time required for the same change in a nitrogen sample of known oxygen content.

Conclusions

The acetone fluorescence test for oxygen is evidently most adaptable to the detection of minute traces of oxygen in other gases. The test is so extremely sensitive that all joints and stopcocks must be air-tight. Whenever possible, it is preferable to seal off the reaction cell rather than to trust stopcocks.

The method is adaptable to the estimation of quantities of oxygen much smaller than can be determined by any of the usual tests. The accuracy is not claimed to be extremely high, but the method should prove of value for the conditions stated. The fluorescence test is not recommended for quantities of oxygen large enough to be accurately determined by the Hempel method.

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Received December 18, 1934. Presented in part before the Division of Physical and Inorganic Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 11 to 15, 1933.

The ultimate object of all research is twofold: to increase the earning capacity of the corporation or individual, and to fulfill the obligation of all really important business organizations—to contribute something constructive to society.

F. O. Clements

A Six-Atmosphere Mercury Manometer

Walter Scholl and R. O. E. Davis

Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

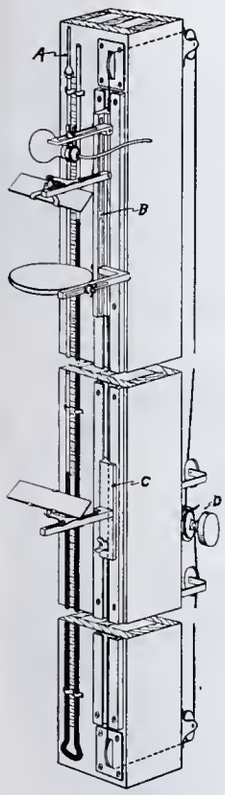

Figure 1

In measuring vapor pressures over solutions of urea and liquid ammonia, a simple mercury manometer capable of measuring pressures up to six atmospheres was constructed. A method for reading the manometer was provided by the use of a periscopic arrangement consisting of a sliding unit, with a light, a mirror, and a reading glass, mounted to reflect the image of the mercury meniscus downward to another mirror conveniently placed for observations. The assembled manometer is shown in perspective in Figure 1.

The wooden post 13 cm. square, as shown at the end section, was made up of five 2-cm. white pine boards. A beam of this construction was found to be free from warping and had very little bending movement. The Pyrex U was made of tubing 6 mm. outside diameter and 4 mm. inside diameter and the two parallel arms were so spaced as to be close to the scale, mounted between them. The scale was made up from selected wooden meter sticks carefully jointed so as to eliminate, as far as possible, any large corrections. The scale was compared with a Bureau of Standards calibrated steel tape. For convenience in reading, a paper scale was prepared from millimeter coördinate paper, by printing the total millimeters in a horizontal position at each centimeter of length. The paper scale was shellacked to 2.5-cm. wooden strips and mounted to the right of the mercury U. The strips should be boiled in paraffin to prevent warping.

A track in the form of a T channel, for the accommodation of the slide units B and C, was mounted to the right of the manometer. The track was made by assembling several brass strips: first the base plate (50 × 3 mm.), attached to the beam with screws, and then the spacers (14 × 7 mm.) and face plates (19 × 3 mm.) attached to this by machine screws at frequent intervals to prevent bending the slides. The unit C, a steel piece 17 cm. long, carried a slotted arm to which was attached the lower mirror, and was provided with a thumb screw for locking it in position.

The unit B was a slotted steel piece 38 cm. long and provided for mounting the second mirror at 180° to the first and 45° to the plane of the supporting beam. On this unit also was attached a 25-watt bulb blackened so as to illuminate the manometer and scale only and placed just above the mirror. Below the mirror was a 12.5-cm. reading glass adjusted to the focal length, about 15 cm. from the mirror. To the upper and lower ends of unit B were attached the ends of a length of picture wire used in moving the unit. The picture wire passed over four brass pulleys at the top and bottom, and opposite each other, on the front and back faces of the beam. The wire made several turns on a brass drum, shown at D, which when turned supplied sufficient friction for moving the unit B in any desired direction. To the drum was attached a ratchet and a wooden hand-hold mounted on the end of the axis. The ratchet held B at any desired position.

The manometer and attachments were mounted on the wooden beam before raising to the vertical position and adding the mercury. To the top of the U at A was attached, by means of a metal joint (*1*) supported by a clamp, a copper tube through which the gas pressure to be measured was applied. The other side of the U connected to a trap, not shown in the figure, for mercury inadvertently forced out of this arm. Three thermometers, placed at equal intervals along the side of the mercury U, were used for making the necessary temperature corrections. The manometer as constructed had an accuracy of ±2 mm. at 5 atmospheres pressure.

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Received December 19, 1934.

Preparation of Sintered Glass Filters

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In many cases in which sintered glass filters[1] are highly useful, very fine grades and carefully standardized porosities are not necessary. If, in addition to this, the diameter of disk need not exceed about 15 mm., it has been found very easy to make such filters directly in the flame of an air-gas blast lamp. Various investigators are making such filters for their own use as aërators and for other simple requirements, but it seems desirable that the method be recorded in the literature.

The chief field of use of such filters in this laboratory has been in the form of filter sticks similar to those described by Kirk (*1*). This apparatus is made by blowing on one end of a thick-walled capillary tube a small thin-walled bulb which is filled with ground glass, mounting the tube in a stirring motor in a vertical position with the bulb down, and rotating the tube in a moderate air-gas blast burner flame for about 10 minutes. If the flame is properly adjusted, the ground glass will sinter through without fusing the bulb walls. The glass should scarcely be red during the heating. After cooling, the end of the bulb is ground away, preferably on a slow-speed silicon carbide wheel, until the sintered disk is of proper thickness.

For making larger diameters of filter, the process is essentially the same, except that the tube is of the correct size for the filter desired. Instead of having a bulb on the end it is simply pulled off in a flame until it is roughly squared across the end, leaving the walls thin, after which the powdered glass is poured in and sintered as described, followed by grinding off the end. For larger filters the heat must be a little more intense.

Either Pyrex brand chemical or soda glass may be used, though the former yields the better results. The glass powder may be of any size desired, but not finer than about 200-mesh. For aërators, coarse filters, and the like, 100-mesh is satisfactory, though finer may be used. The filter sticks are most satisfactorily used with asbestos as described by Miller and Kirk (*3*), and are of the greatest utility when so employed. Another valuable application is in the filtration

[1] Manufacture of sintered glass filters is covered by patents held by Schott & Gen., in the United States by Patent No. 1,620,815.

of mercury, as, for example, spraying it into a washing tower. In this case about a 40-mesh glass should be used. An extremely rapid filtration is obtained with the delivery of a mercury cloud, the particles of which are individually barely visible. While not so universally applicable as the method described by Kirk, Craig, and Rosenfels (*2*), this method should be of considerable value in solving many special problems arising in the research and analytical laboratory.

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Use of Sintered Glass Disks in Distillations

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THE writer has had occasion to extract material with large volumes of volatile organic solvents. When the extract, containing a high percentage of oily and other matters, was concentrated by distilling the volatile organic solvents, considerable difficulty was experienced in preventing bumping. The common expedients, such as putting in glass beads, pieces of porcelain, pumice, and capillary tubing, were found to be of little aid.

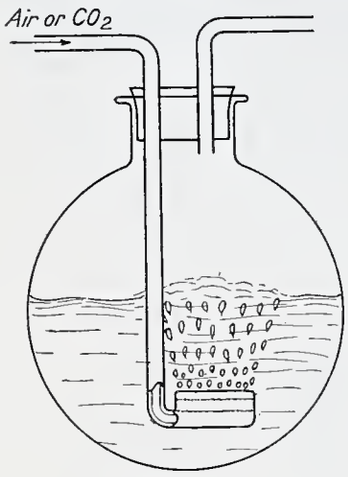

Figure 1

The incidence of bumping was completely eliminated by introducing a sintered filter disk as shown in the diagram. (Such glass tubes are sold commercially under the name of "gas distribution tubes with fused-in fritted-glass filter disks.") Air, passed through the tube, is broken up into many tiny bubbles which keep stirring the solution, thus preventing local superheating. When the solvent has been almost all distilled and a fresh charge of extract put in, the whole is effectively mixed by allowing air to be blown more rapidly through the solution, thereby obviating the necessity of disengaging the flask from its clamped position and rotating or shaking to effect mixing. Several fresh charges have been added to the original one by this method without disturbing the distilling flask. Despite the increasing concentration of oily matters, there was no bumping at any stage.

In certain cases where air is not desirable because it may oxidize the extracted matter, or induce chemical change, an inert gas like nitrogen or carbon dioxide may be used.

It is suggested that heated gases be used to distill the solvents instead of an outside source of heat. Steam distillation also has been carried out smoothly and effectively by leading the steam through the sintered glass disk.

Received January 12, 1935.

A Simple Inexpensive Galvanometer Suspension

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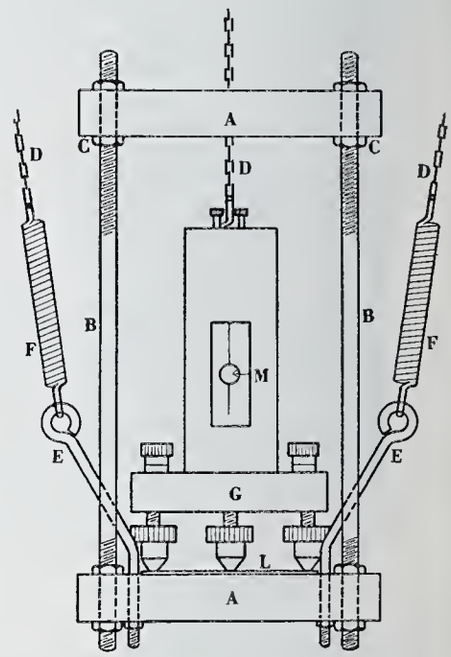
IN THE course of recent work it was found necessary to insulate thoroughly a high-sensitivity galvanometer (Leeds & Northrup Co., Type HS) from all mechanical shock.

This was accomplished with the modified Julius suspension shown. The heavy soapstone slabs, *A*, are separated by the threaded rods, *B*. The slabs are free to move vertically and can be held in any position by means of the lock nuts, *C*. The galvanometer, *G*, rests on a sheet of tin plate, *L*, which is set on the base block. The tin plate is grounded through a flexible lead and acts as an electrostatic shield for the galvanometer. The legs of the galvanometer rest upon small blocks of paraffin.



The whole is supported by the three eyebolts, *E*, spaced at the corners of an isosceles triangle. These are connected through the springs, *F*, to the supporting dog chain, *D*. All electrical connections are made by wires dipping into 30-cc. beakers containing mercury, mounted on small paraffin blocks placed on the base block. Mercury is used because it allows the use of large lead wires and at the same time prevents the transmission of any mechanical disturbances through the leads to the galvanometer. It was found that when the galvanometer was enclosed in a large metal compartment with a glass door, the absolute lack of air currents made the customary damping vanes of the Julius suspension unnecessary. The metal of the box made an efficient electrostatic shield when grounded.

In operation the upper soapstone slab is raised or lowered until the center of gravity of the system is at the mirror, *M*, of the galvanometer. Under these conditions the system will rotate about this point and the mirror will be at the point of least motion of the system. Then, with the springs absorbing all vertical impulses and the chain the horizontal ones, with the system once in equilibrium, the mirror will not be disturbed by outside mechanical forces. This condition has been realized in actual operation.

This suspension has proved satisfactory in measuring deflections of 0.1 mm. on a scale placed at 1 m. with several large electric motors operating very close to the galvanometer.

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[1] Present address: The Atlantic Refining Co., Franklin, Pa.

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HARRISON E. HOWE, EDITOR

Determination of Active Ingredients and Total Fatty Matter in Sulfonated and Sulfated Oils

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THE test for fatty matter is considered the most important determination in the analysis of sulfonated oils, primarily because the price of the oil is based upon it. This determination has consequently been the subject of considerable investigation for a good many years, with the result that a number of methods have been proposed, many of which are in use but unfortunately do not always yield concordant results. In response to a questionnaire addressed to mill and commercial laboratories and to manufacturers of sulfonated oils, Grimshaw (*4*) reports as many as 25 methods in use, giving results which in some cases differed by more than 10 per cent. Fahrion (*3*) analyzed a sample of sulfonated castor oil, containing about 80 per cent fatty matter, by three accepted methods and found that the results varied by as much as 4.7 per cent. Within the past few years attempts have been made by several technical and trade associations to standardize this test, among them the American Association of Textile Chemists and Colorists (A.A.T.C.C., *6*). The sulfonated oil committee of this association has investigated several of the more reliable methods and has also proposed a new method, called the total active ingredients method. The proposed method not only yields the true fatty matter but is also applicable to true sulfonated fatty or mineral oils—that is, oils which are not decomposed by boiling with mineral acid—in which cases the other methods are useless. In this paper the results of an investigation of the Wizoeff, Herbig (Bureau of Standards), and total active ingredients methods are reported and compared.

Herbig and Wizoeff Methods

Upon sulfonating castor oil in the usual manner, some of the glycerides are hydrolyzed into free fatty acids, which subsequently are more or less polymerized. As far as the fatty matter itself is concerned, sulfonated castor oil may be considered to consist of glycerides, free fatty acids, and polymerized oil. According to Richardson and Walton (*10*), the glycerides in ordinary sulfonated castor oil consist mostly of diricin olein with some triricin olein. There is probably also present a sulfonated monoglyceride, which, however, is very unstable. The most important polymer is ricino-ricinoleic acid, an ester formed from two molecules of the fatty acids with the elimination of water:

$$2[C_6H_{13}\underset{\underset{OH}{|}}{C}HCH_2CH{:}CHC_7H_{14}COOH] =$$

Ricinoleic acid

$$C_6H_{13}\underset{\underset{OH}{|}}{C}HCH_2CH{:}CHC_7H_{14}\overset{\overset{|}{C}}{O}O \qquad C_6H_{13}CHCH_2CH{:}CHC_7H_{14}COOH + H_2O$$

Ricino-ricinoleic acid

Higher polymers of the same type, having the general formula $OH(C_{17}H_{32}COO)_nC_{17}H_{32}COOH$, have also been reported in the literature. Lactones, lactides, anhydrides, and similar polymers (*2*, *10*) are generally assumed to be absent in the original oil or present in negligible quantities, but lactides may be formed upon boiling with mineral acids.

HERBIG METHOD. In the original Herbig method (*8*), which is the same as the Bureau of Standards method (*1*), the sample is boiled with strong hydrochloric acid (sp. gr. 1.19) for 15 minutes, the fat is then extracted, the solvent evaporated, and the residue dried at 105° to 110° C. Upon boiling with mineral acids, hydrolysis of the glycerides as well as polymerization of the fatty acids take place, giving low results for the fatty matter to the extent of the loss of glycerol in the first reaction and of water in the second. Hence any method based on acid decomposition alone is bound to give low results, which moreover may vary within certain limits, as will be shown below, with the method of decomposition.

In the author's work it was found that heating for 15 minutes was insufficient, since both the oil and water layers remained turbid, indicating incomplete decomposition. The heating was therefore continued for 1.5 hours, when both layers were entirely clear. In another series of tests with this method, the strong hydrochloric acid was replaced by 25 cc. excess of *N* sulfuric acid, above the amount required to neutralize the soap in the sample. The method with this modification is designated as the Herbig-A.A.T.C.C. method. The rest of the procedure was the same as the original Herbig method, with the further exception that the decomposition was carried out in an Erlenmeyer flask provided with a reflux condenser.

WIZOEFF METHOD. In the official method of the Wissenschaftliche Zentralstelle für Öl und Fettforschung (*12*) the

sample is boiled for over an hour with 50 cc. of strong hydrochloric acid, the fatty matter extracted and saponified with alcoholic potassium hydroxide, and finally the fatty acids are determined in the soap solution in the usual way. A number of investigations (*9*) have shown that sulfonated castor oil, as well as its acid-decomposed fatty matter, may be completely saponified, including the polymers. Saponification of the fatty matter must necessarily be accompanied by loss of glycerol from the glycerides and a gain of water due to the splitting of the polymers. Hence results by saponification methods may or may not correspond to the true weight of fatty matter in the original sample, depending upon whether or not the loss of glycerol is balanced by the gain of water absorbed by the polymers.

Total Active Ingredients Method

The total active ingredients method, suggested by the writer, was originally developed by the A.A.T.C.C. committee (*5*) on sulfonated oils in connection with the determination of organically combined sulfuric anhydride. It consists essentially of extracting the original sample with a solvent over concentrated salt solution, purifying the extract, and weighing the residue. The fatty matter, which is considered to be practically unchanged in composition and weight from that in the original sample and consequently may be designated as true fatty matter, is obtained from the residue by subtracting the organically combined sulfate group, which is nearly always determined in the analysis of a sulfonated oil. With some highly sulfonated oils, a middle layer is formed upon extracting with ether; hence some changes in the regular procedure were found necessary in such cases.

Procedures

Ordinary Sulfonated Oils. Weigh enough of the sample to yield about 5 grams of anhydrous fat into a 250-cc. pear-shaped separatory funnel containing 50 cc. of a saturated solution of sodium chloride, some solid salt, 5 drops of a 0.1 per cent solution of methyl orange, and 50 cc. of ether. Decompose the soap with approximately *N* sulfuric acid until slightly acid (about 0.3 cc. excess). After settling for at least 5 minutes (all separations should be allowed to clear for that period), draw off the lower layer into a second separatory funnel and wash the ether layer with 25-cc. portions of the salt solution until practically neutral to methyl orange—i. e., until one drop of 0.5 *N* caustic turns the wash water strongly alkaline. Extract the combined water layers with two 25-cc. portions of ether and wash the latter with salt solution as in the first funnel. Combine the ether layers and shake for about 2 minutes with 10 cc. of 25 per cent solution of sodium sulfate, warmed to 55° C. Allow to settle for about 10 minutes and, to prevent crystallization of the salt, immerse the lower part of the funnel in a beaker of warm water. Draw off the lower layer as completely as possible, transfer the ether layer into a dry 250-cc. Erlenmeyer flask, rinse the funnel several times with ether, and evaporate to about 75 cc. Immerse the Erlenmeyer flask in ice water for 30 minutes, mixing frequently. Filter into a tared 150-cc. beaker, and wash the flask and filter paper with ether until free from fat (absence of oil stains on filter paper upon drying), catching the filtrate if necessary in a second beaker. Evaporate the filtrate to a total volume of about 20 cc., add exactly 2 cc. of 0.5 *N* alcoholic potassium hydroxide, mix by gently swirling the contents, and evaporate on the water bath until practically free of ether. Dry in a hot air oven at 108° to 112° C. for 1.5 hours, cool in a desiccator, and weigh. Repeat heating for 30-minute periods until constant weight is reached.

Highly Sulfonated Oils. Extract the sample once with ether over salt solution and wash the ether layer as above, retaining the middle layer with the ether extract. The combined water layers are extracted twice with a mixture of 20 cc. of ether and 10 cc. of alcohol. The combined ether-alcohol layers are then washed with 25-cc. portions of salt solution until neutral to methyl orange. The extracts are finally combined in the first funnel and washed with 10 cc. of Glauber's salt solution as above. There should be no middle layer at this stage; if one is present, 5-cc. portions of alcohol are added until it disappears completely. The ether-alcohol layer is evaporated, chilled, and filtered as in the regular procedure, except that the filter paper is washed with a mixture of 2 parts of ether to 1 part of alcohol. After evaporating the greater part of the solvent, exactly 1 cc. of 0.5 *N* alcoholic potassium hydroxide is added and the rest of the solvent evaporated on the water bath, evaporation being hastened by stirring with a glass rod, which is tared with the beaker. When practically free of solvent, 5 cc. more of the alkali are added and the residue is heated to constant weight.

$$\text{Correction for alkali added, grams} = \frac{(K-H)}{1000} \times \text{normality of KOH} \times \text{cc. of KOH}$$

$$\text{Corrected residue, per cent} = \frac{(\text{weight of residue minus correction for alkali}) \times 100}{\text{weight of sample}}$$

True fatty matter, per cent = per cent corrected residue minus per cent of organically combined $NaSO_3^-$.

The term $NaSO_3^-$ represents the inorganic group in the total active ingredients in accordance with the formula RO $\boxed{SO_3Na}$ where R represents the fatty radical. The oxygen adjacent to the fatty radical is considered part of the fatty matter, since it is part of the hydroxyl group in ricinoleic acid and cannot readily be removed. The $NaSO_3^-$ is calculated from the per cent of organically combined sulfur trioxide in the original sample as follows:

$$\text{Per cent of organically combined } NaSO_3^- = \text{per cent of organically combined } SO_3 \times \frac{NaSO_3^-}{SO_3} = 1.2875 \times \text{per cent of combined } SO_3$$

The combined salt solutions and the filter paper should show no fat upon acidification and boiling, or at most a trace. If deemed advisable, the salt on the filter paper may be dissolved in hot water, the filtrate added to the salt solutions, and the latter boiled with strong hydrochloric acid for about 1 hour. The fatty matter, if any, is then extracted once with about 30 cc. of ether, the extract washed free of mineral acid, and the residue after evaporating the solvent added to the active ingredients. The addition of alkali is necessary to prevent decomposition of the active ingredients during drying, indicated at first by the residue turning red (owing to methyl orange dissolved in the oil) and later by blackening and charring. In the case of highly sulfonated oil, considerably more alkali is required to render the oil stable to heating. The residue retains traces of alcohol or moisture very tenaciously and 2 to 3 hours' heating is required to obtain constant weight. However, with the quantity of alkali recommended the amount of decomposition is negligible, since 3 to 5 hours' additional heating after constant weight was reached showed no loss in weight and practically no change in the appearance of the oil. Further heating, however, finally caused both charring and loss of weight. It is advisable to evaporate the alcohol as much as possible before the alkali is added; otherwise the residue may jell and slow up volatilization of the solvents.

Results by Total Active Ingredients Method

A sample of sulfonated castor oil was analyzed by this method for true fatty matter by three different men and the results are given in Table I. All acidities in this paper were calculated on the original sample and then converted to milligrams of potassium hydroxide per gram of castor oil fatty acids as determined by the Wizoeff method. The acidity of the original sample represents the free fatty acids plus the fatty acids as soap.

Table I. True Fatty Matter and Acidities by Total Active Ingredients Method

Analyst		Total Active Ingredients %	SO_3 True Fatty Matter %	Acidities, Mg. KOH per Gram Fatty Acids: In true fatty matter	In original sample
1		71.32	...	...	...
2		71.43	...	...	...
3		71.29	...	...	...
	Av.	71.35	64.65	117.6	119.2

The small drop from the original acidity indicates that the total active ingredients had probably undergone very little change during extraction and heating. Table II shows that the total is within 0.2 per cent of 100 per cent.

For further determination of the purity of the total active ingredients, the following additional tests were applied:

Fatty Matter. The fatty matter in the total active ingredients was determined by the Herbig-A.A.T.C.C. method and was found to check with the fatty matter in the original sample obtained by the same decomposition method. This was to be expected from the fact that the wash waters and salts upon the filter paper upon decomposition with acid and boiling showed only a trace of fat.

Combined Sulfuric Anhydride. There was no decomposition of the sulfonated oil, since the combined sulfur trioxide in the total active ingredients determined by the A.A.T.C.C.-acid titration method (*7*) agreed with the value obtained on the original sample.

Foreign Salts. The organically combined sulfur trioxide was determined also by the A.A.T.C.C.-gravimetric method (*5*, *7*), which again checked with the original sample. Evidently the presence of foreign salt would have been indicated by a high result. The absence of foreign salt was also shown from the fact that upon chilling the residue after almost complete evaporation of the solvent before the addition of alkali, no separation occurred.

Solvent. The absence of solvent was proved by the fact that additional heating for over 4 hours at 110° C. had practically no effect on the constant weight.

Table II. Complete Analysis of Sample of Sulfonated Castor Oil

	%
Moisture	25.1
Inorganic salts	0.9
(Na-H) as soap	1.2
Free glycerol	1.2
Total active ingredients	71.4
Total	99.8

Results by Different Methods

The same sample was analyzed also by the Herbig-A.A.T.C.C., Wizoeff, and Herbig methods and the results, which are the averages of a number of tests, are listed in Table III.

It will be noticed that the total active ingredients method gave the highest result and the Herbig method the lowest—namely, 64.65 per cent compared with 62.63 per cent, or a difference of 3.3 per cent on the fat basis. The drop in acidity from 119.2 to 96.1 mg. in the Herbig method indicates that the low result in fatty matter is probably due to polymerization whereby water is eliminated. Undoubtedly there was also some loss of glycerol. Upon comparing the Herbig-A.A.T.C.C. method with the Herbig method, the fatty matter was 63.68 and 62.63 per cent, respectively, and the acidity 133.0 and 96.1 mg., respectively. It is thus evident that the results by decomposition methods alone may vary with the conditions of decomposition. In the Herbig-A.A.T.C.C. method, where dilute acid was used, there was evidently more hydrolysis of the glycerides than polymerization of the fatty acids, since the acidity is above the original sample; the reverse was true in the Herbig method. Both reactions must have occurred to a lesser extent in the Herbig-A.A.T.C.C. method, as the fatty matter by this method is more than 1 per cent greater than by the Herbig method.

The fatty matter by the Wizoeff method lies between the two Herbig methods. Since the Wizoeff result represents the pure fatty acids, the higher result by the Herbig-A.A.T.C.C. method definitely indicates the presence of glycerides, and the lower results by the Herbig method, polymers. The acidity of the fatty acids was made also before drying and was found to be 188.4 mg., compared with 184.2 mg. after drying for 2 hours at 100° to 105° C. The former is practically the theoretical neutralization value for castor oil fatty acids. Winokuti (*11*) found, upon heating castor oil fatty acids for 5 hours, that the acidity dropped only 0.3 mg. at 50° C. but 14.0 mg. at 105° to 110° C. The Wizoeff method yields a definite chemical compound—the pure fatty acids—and with care concordant results are readily obtained. The main objection to this method is that the results may vary, as already stated, from the true amount of fatty matter present in the original oil. In the case of this sample, the fatty matter by this method was 2.3 per cent below the true fat as determined by the total active ingredients method. The difference may be even greater for a sample both high in glycerides and low in polymers, as, for example in a low sulfonated olive oil.

It will be observed that the highest result was obtained by the total active ingredients method. Unless splitting of the polymers occurs, which is considered not probable in acid solutions, the method yielding the highest result of fatty matter must necessarily be the nearest to the true content of fatty matter. Hence the fatty matter by the total active ingredients method is considered the most accurate of the methods tested. Similarly, the order of diminishing accuracy of the other methods is considered to be Herbig-A.A.T.C.C., Wizoeff, and Herbig.

If $NaSO_4^-$ is subtracted from the total active ingredients instead of $NaSO_3^-$, the result for the sample analyzed checks closely with the Herbig-A.A.T.C.C. method. Whether or not this happens to be merely a coincidence was not determined. It was also noticed that higher results were obtained by the original Herbig method, in which boiling with strong hydrochloric acid is continued for only 15 minutes, than when boiled for 1.5 hours—undoubtedly because of less polymerization and hydrolysis. However, the turbidity of the contents after the short heating makes this procedure uncertain. The total active ingredients method was used to determine the fatty matter in samples of sulfonated olive oil, sulfonated tallow, highly sulfonated castor oil, true sulfonated fatty oil, and sulfonated mineral oil, and the results were found to be as satisfactory as the analysis of the sample of sulfonated castor oil reported in this paper.

Table III. Comparisons of Fatty Matter and Acidities Determined by Different Methods

Method	Fatty Matter %	Diff. %	Fatty Matter Based on T.A.I. Method %	Diff. %	Acidities, Mg. KOH per Gram Fatty Acids
Original sample	....	...	....	..	119.2
Total active ingredients (T.A.I.)	64.65	...	100.0	..	117.5
Herbig-A.A.T.C.C. (dilute acid)	63.68	0.97	98.5	1.5	133.0
Wizoeff	63.18	1.47	97.7	2.3	184.2
Herbig (strong acid)	62.63	2.02	96.7	3.3	96.1

Summary

The fatty acids or Wizoeff method for the determination of total fatty matter in sulfonated oils and the Herbig (Bureau of Standards) or acid-decomposition method were found to yield low results. Furthermore the Herbig method is subject to variations, depending upon the method of decomposition; stronger acid and continued boiling yield the lower results, probably due to increased hydrolysis and polymerization. A new method is proposed, called the total active ingredients method, which is considered to give the most accurate values. It consists essentially in separating and weighing the pure, undecomposed sulfonated oil. As a rule the results are higher than by the other methods. The weight of the fatty matter by this method corresponds to the true fatty matter in the original sample. The new method is also applicable to true sulfonated fatty and mineral oils, in which cases the other methods are useless as these oils are not decomposed by acids.

Acknowledgment

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A Standardized Test of Gasoline Color Stability

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While the bulk of the gasoline now sold is dyed, much is marketed water-white. Many gasolines which are colorless or nearly so when delivered to the filling station become discolored on exposure to strong light. This is particularly undesirable if the gasoline is to be dispensed in pumps with visible bowls, in which it may be exposed for considerable periods to daylight or even to direct sunlight. Before shipping, therefore, gasoline is often subjected to a test of its color stability, although this is not required by specifications, to determine whether it can be exposed to light without darkening.

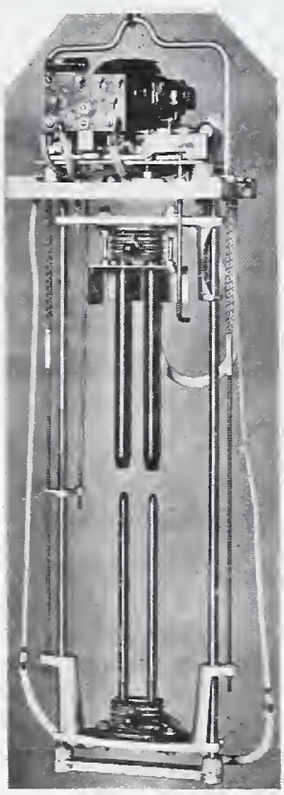

Figure 1. Carbon Arc Lamp

The usual test of color stability is exposure of the gasoline to sunlight. There are, however, no generally accepted conditions for making the test. Sometimes the exposure is for a period of 2 hours, sometimes 8, or even longer. The container used may vary in size from a 113-cc. (4-ounce) bottle to a 37.85-liter (10-gallon) bowl. It is obvious, moreover, that "sunlight" is far from being a uniform illumination. The light from the sun varies in intensity and in spectral distribution of energy from hour to hour, from season to season, and from place to place.

A step toward precision in sunlight testing was made by Beard and Reiff (*1*) when they used an oxalic acid–uranyl acetate actinometer to measure the intensity of sunlight in order that each test sample might be subjected to the same amount of radiation. Hoeman (*5*) gaged sunlight exposure by the time of reduction of a ferric oxalate actinometer. He did not show, however, that the light which affected the actinometer was precisely that which caused the darkening of gasoline. These methods of measurement, even if accurate, do not eliminate all the disadvantages of a sunlight test, as sun exposure can be made satisfactorily only in the middle of the day, not at all on cloudy days, and with difficulty in the weak sunlight of winter. Moreover, the length of time required when the sun is used as the light source, being a matter of hours, is inconvenient.

A satisfactory test of color stability should use a light of unvarying intensity and of sufficient strength to make possible a test of short duration.

Apparatus

These requirements are fulfilled, in the test to be described, by exposure to light from a carbon arc.

The light source used is a flame-type carbon arc, type C3A of National Carbon Company, pictured in Figure 1. It is a 60-ampere, 50-volt, vertical trim lamp, operating on alternating current, the carbons being fed automatically by an electric motor. The lamp, as manufactured, has two upper carbons 22 mm. in diameter and two lower 13-mm. carbons. The two pairs of carbons burn alternately, the arc shifting from one to the other every 20 to 30 minutes. The sizes are so proportioned that upper and lower carbons burn at the same rate, and the position of the arc does not change. Much of the work to be described was done with the lamp as purchased, and satisfactory results were obtained. However, the changing of the arc flame from one pair of carbons to the other during the period of exposure resulted in the illumination received by samples in different positions around the lamp being not quite the same. To increase the uniformity of illumination and the precision of the test, one pair of carbons was removed and the remaining pair placed in the exact center of the frame. The lamp was encased in a heavy sheet-metal housing, which is shown in plan in Figure 2. The samples were placed in slots in the housing, and these slots were water-jacketed to minimize rise in temperature. The center of each bottle was 30.5 cm. (12 inches) from the center of the arc, and no slots were placed where the shadow of the arc guide rods could fall upon them. The apparatus was connected to an efficient suction line, which served to create a draft, cooling the instrument and carrying off the gases produced.

Coblentz, Dorcas, and Hughes (*2*) have reported that the carbon arc "of all the artificial illuminants tested is the nearest approach to sunlight." A mercury arc lamp was used at the beginning of this study, but the carbon arc is preferred because of its uniformity and the closer resemblance of its illumination to sunlight. The arc was fitted with the "sun-

shine carbon," a cored carbon containing cerium, that gives a light similar to sunlight (*3*, *4*) having a practically continuous spectrum from 2800 Å. through the longer wave lengths. In Figure 3 light from the arc is compared with average sunlight. The main difference between the two sources of illumination is the presence of a greater amount of short ultraviolet light in the arc spectrum than is present in that of the sun. Much of this light was filtered out by the glass in the tests made in glass bottles, but it was present when the testing was done in quartz containers.

Standardization of Test

As standard of reference for the arc test, the color drop of gasoline when exposed to the brightest summer sun was used. Samples of many gasolines were exposed to the sun on clear and cloudless days in July and early August. The rates of color change were measured and an exposure to the artificial light found which would give a color drop equal to that produced by the sun in a given period. The intensity of the sunlight was followed by measuring the rate of decomposition in an oxalic acid solution containing uranyl acetate (oxalic acid actinometer, *6*) during the exposures, in order to make sure that there was no great variation in the sunlight on the different days on which the work was done. No results were discarded on the basis of actinometer measurements, so that the results represent average values for bright summer days.

In making a comparison of the effects of the sun and of the arc, a sample of gasoline in a 113-cc. (4-ounce) oil sample bottle was exposed to sunlight, beginning at noon, and its color on the Saybolt scale read every 10 minutes. At the same time samples of the same gasoline were exposed to the arc in bottles of ordinary glass, of Corex D glass (an ultraviolet transmitting glass of the Corning Glass Company), and of quartz, and the color was read every 5 minutes. To insure uniformity, the glass bottles used were all taken from a single shipment from the manufacturer. They had an average wall thickness of 0.16 cm., and measured in an ultraviolet spectroscope showed total extinction of light of wave length below 3200 to 3300 A. The Corex D bottles were made up from tubing, had a wall thickness of 0.24 to 0.30 cm., and in the spectroscope showed partial extinction of light at 2800 to 2900 Å. and considerably lessened transmission at shorter wave lengths. The quartz bottles were 0.12 to 0.16 cm. in wall thickness and were transparent to ultraviolet as well as visible light.

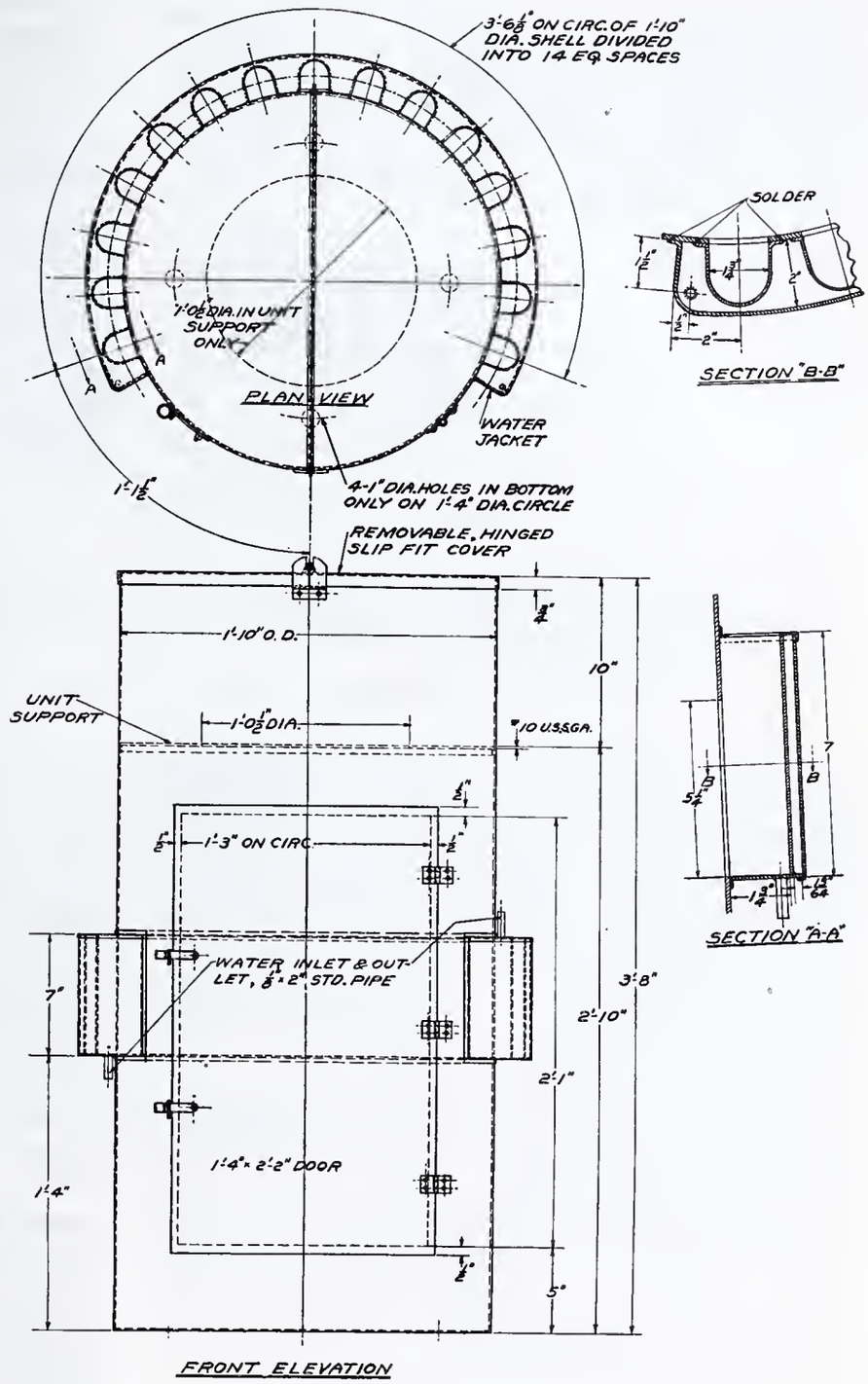

FIGURE 2. PLAN OF ARC HOUSING

Shell, cover, door, and water-jacketed sample holder made of No. 18 U. S. Standard GA galvanized sheet steel. Soldered construction throughout.

TABLE I. COLOR CHANGE IN GASOLINE EXPOSED TO SUN AND ARC

	West Texas Gasoline			Commercial Gasoline B			
Time, min.	Sun, glass	Arc, glass	Arc, quartz	Sun, glass	Arc, glass	Arc, quartz	Arc, Corex-D
0 (initial)	22	22	22	23	23	23	23
5	..	18	18	..	20	20	20
10	21	17	11	23	20	20	20
15	..	15	3	..	19	18	18
20	19	13	3	22	18	17	18
25	..	12	3	..	18	16	17
30	18	12	3	22	17	16	16
35	..	9	3	..	17	14	16
40	17	9	3	20	16	12	15
50	16	..	..	20	..	..	..
60	15	..	..	19	..	..	..
90	9	..	..	..	..	..	..
120	9	..	..	17	..	..	..
180	..	..	..	17	..	..	..
24 hours	..	..	..	17	..	..	..

Typical results of exposure to the sun and arc are given in Table I.

The first of these gasolines was unstable, the second fairly stable. Similar comparisons were made with 20 other gasolines. Some were commercial gasolines purchased at filling stations, probably blends of straight-run and cracked products, while others were cracked gasolines produced in experimental units from a variety of charging stocks. Nearly all the gasolines which were specially prepared for this study were refined with sulfuric acid.

As a rule it was found that when a gasoline contained in a glass bottle was exposed to the sun, there was at first a fairly rapid acquiring of color (which might be preceded by a short induction period) as measured by lowering of the reading on the Saybolt scale. After this initial stage, which usually lasted considerably less than 2 hours, the rate of drop in color was much less. After 2 hours, the change was very slow. On exposure to the arc in a glass bottle, the color

change followed the same course, being first rapid and then slow, though the darkening took place at a much faster rate than in the sun. In a Corex D bottle the darkening was still more accelerated, and went on most rapidly in a quartz bottle. In addition, in quartz the rate of change often did not greatly diminish after the initial rapid phase, as it did in a glass bottle in either the sun or arc.

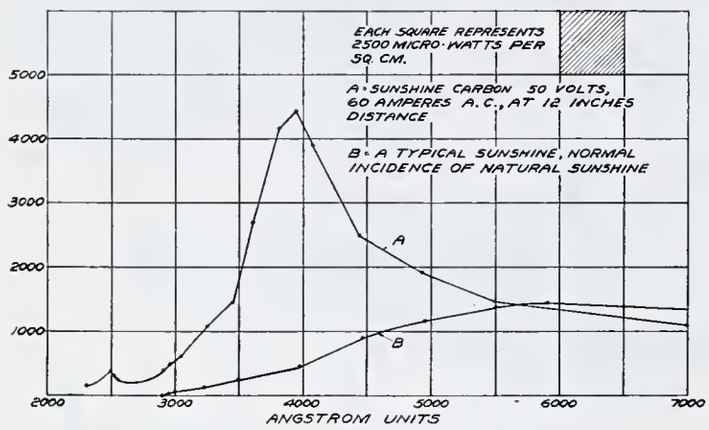

FIGURE 3. COMPARISON OF LIGHT FROM ARC AND SUN

In Table II are shown under "Major Color Change" the period required by each gasoline to drop to the color indicated on sun and on arc exposure. The data show that most of the drop in color occurs in a considerably shorter time than 2 hours in the sun, after which there is practically no change. The rates of color change in sun and arc are different for different gasolines in the early part of the exposure. However, as indicated in the last three columns, after 120 minutes in the sun or 40 minutes in the arc the colors are nearly the same, the variations in the early part of the exposure having been equalized by exposing for a longer period.

As has been mentioned, color change is very slow after 2 hours' exposure to bright summer sun. It was decided to adopt this period of exposure to sunlight in a glass bottle as the standard interval, and from comparison of the rates of darkening on sun and arc exposure, the effect produced on color by the sun in this time is found to be closely approximated by 40 minutes' exposure to the arc at 30.5 cm. (1 foot) distance. Twenty-five minutes' exposure to the arc in Corex D or 15 minutes in quartz, as figures given in Table IV show, give almost exactly the same results as 40 minutes in glass.

Effect of Temperature

Although reactions which are primarily photochemical are not significantly changed in rate by slight variations in temperature, it was considered desirable to maintain a uniform temperature in this test. The bottles containing the gasoline samples are cooled by a water jacket during exposure to the arc. The cooling minimizes temperature variation and checks loss of light ends.

To determine whether such temperature variations as might occur during routine use of this test would affect the results, comparative tests were made, in some of which the bottles were cooled as usual, and in others no water was circulated through the jacket, which allowed the gasoline to become warm.

The tests were of 40 minutes' duration in glass bottles and 15 minutes in quartz. The results are shown in Table III.

The slightly lower colors, when the samples were not cooled, are due to loss of light ends, which is appreciable when the bottles become warm. The sample of West Texas gasoline exposed without cooling, of 22 color, was made up to its original volume with 30 color gasoline and then was 24 color, the same as the samples exposed with cooling. The variation in final colors caused by much greater temperature variation than would ever occur in the normal use of this test is slight. It is believed that errors caused by temperature differences, if the method is used as described, will be negligible.

As a final check on the accuracy of the accelerated test, comparisons are given in Table IV of the colors of 24 gasolines at the end of the test periods proposed.

TABLE II. COMPARISON OF COLOR DROP IN EXPOSURE TO ARC AND SUNLIGHT

Origin of Gasoline	Original Color	Color after exposure	Major Color Change: Time in sun Min.	Major Color Change: Time in arc Min.	Color after 120 Min. Sun	Time to Same Color in Arc	Color after 40 Min. Arc
Midcontinent	30	27	40	20	26	30	26
West Texas	30	25	90	30	24	35	23
Kentucky	29	26	40	15	25	40	25
Peruvian	29	27	40	10	26	15	25
California	28	19	40	30	17	45	18
Commercial A	27	21	80	25	18	Over 40	20
Pennsylvania	26	24	40	25	23	35	23
Commercial E	25	19	40	15	18	25	16
Blend F	24	7	80	25	0	Over 40	3
Commercial B	23	18	80	20	17	30	16
West Texas	22	15	60	15	9	35	9
Commercial C	22	2	80	30	−5	Over 40	0
Commercial D	21	13	50	30	12	30	12

TABLE III. EFFECT OF TEMPERATURE

	With Cooling	Without Cooling
Exposure, 40 minutes in glass		
Pennsylvania blended gasoline		
Original color	27	27
Color after exposure	17	16
Final temperatures, ° C.	48	84
West Texas cracked gasoline		
Original color	30	30
Color after exposure	24	22
Final temperature, ° C.	45	56
Exposure, 15 minutes in quartz		
Midcontinent		
Original color	30	30
Color after exposure	17	18
Final temperature, ° C.	44	57
California		
Original color	27	27
Color after exposure	26	25
Final temperature, ° C.	44	57

TABLE IV. COLOR OF GASOLINES AFTER EXPOSURE

Origin of Gasoline	Initial Color	Color, Saybolt after Exposure to: Sun in glass 120 Min.	Arc in glass 40 Min.	Arc in Corex-D 25 Min.	Arc in quartz 15 Min.
Midcontinent	30	26	26	..	..
West Texas	30	25	25	..	..
Blend A	29	25	25	..	..
Peruvian	29	26	25	..	25
Kentucky	29	25	25	..	22
California	29	21	23	..	..
Texas	28	23	..	22	23
California	27	25	..	23	25
Commercial A	27	18	20	19	20
Pennsylvania	26	23	23	..	..
Blend B	26	..	22	24	24
Blend C	25	17	16	17	18
Blend D	25	..	17	21	18
Blend E	24	..	21	21	22
Blend F	24	0	3	12	16
Commercial B	23	17	16	17	18
Commercial C	22	−5	0	−3	1+
West Texas	22	9	9	..	3
Commercial D	21	12	12	..	12
Blend H	21	..	19	20	19
Blend I	20	..	18	19	20
Blend J	19	..	17	17	18
Montana	19	13	..	13	15
California	17	14	..	13	14

On most samples there is little variation in the final results between the testing in bright sunlight, or by exposure to the arc in glass, quartz, or Corex D bottles.

Conclusions

As a reproducible test of color stability of gasoline, exposure to a carbon arc burning "sunshine" carbons using 60 amperes at 50 volts alternating current is recommended.

In the latitude of Chicago, 40 minutes' exposure at 30.5 cm. (1 foot) distance from this arc is equivalent, in the change in color produced, to a 2-hour exposure to brightest summer sun, the samples in both cases being in glass bottles. This is a sufficiently long exposure to differentiate between stable and unstable gasolines, and after this period further drop in color is usually slow. For routine work, further acceleration and nearly as accurate results may be obtained by using an exposure of 15 minutes in a quartz container or of 25 minutes in one of Corex D. This test has been used in these laboratories for 3 years and has proved rapid and reproducible.

Acknowledgment

The authors wish to express their thanks to Wayne L. Benedict for assistance in the experimental work.

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Determination of Alpha-Amylase

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In revising the method of Jozsa and Gore for the determination of liquefying power, the authors have improved the experimental technic and standardized the liquefying curve. By introducing a new type of enzyme unit termed the liquefon, they have been able to calculate accurate values for alpha-amylase activities from the measured amounts of liquefied starch. The enzyme-unit method of expression is of general applicability and has been successfully applied to the study of other enzymes.

During the last few years several investigators have studied the liquefying action of alpha-amylase on gelatinized starch.

Jozsa and Gore (*6*) have published a method for the determination of the liquefying power of malt diastase, based on viscosity measurements of a remarkably uniform starch paste, which enables rather accurate measurement of the amount of starch liquefied when alpha-amylase acts on the starch paste. However, they applied their experimental results rather inaccurately when they assumed that the liquefying power of a given malt was proportional to the amount of starch liquefied under the experimental conditions. This assumption leads to erroneous activity values unless the experimental range is narrowly limited. Fletcher and Westwood (*1*) have suggested the use of a restricted range, but this is not all satisfactory. Other workers (*7*) have proposed a rather complete modification, but their method of calculating activity values is not sound. They report values for the liquefying power of a pancreatin preparation which deviate from one another as much as 10 per cent. These deviations may be due to their method of calculation, which apparently involves an empirical determination of certain constants for a given preparation and then the extension of these constants to any alpha-amylase preparation. This extension is certainly not accurate because of wide deviations in the rate curves of various preparations, particularly when the substrate is largely converted. Their expression of liquefying power is also inaccurate, since it represents only an average value for the rate of conversion of substrate and is not proportional to the actual enzyme content—that is, a doubling of enzyme content would not double the liquefying power of the preparation as measured by them.

In view of the above, a fundamental revision of the method is certainly necessary. The authors believe that the revision herein proposed enables one to measure accurately the activity of an alpha-amylase preparation.

In order to calculate the concentration of alpha-amylase in a given enzyme preparation from the amount of starch liquefied under the specified conditions, the authors have introduced a new enzyme unit, the "liquefon," defined as that amount of starch-liquefying enzyme which will convert the standard starch paste at the rate of 25 mg. of dry starch per minute at zero time under the given experimental conditions. Since the rate at zero time is directly proportional to enzyme concentration, the number of liquefons per gram of preparation is an exact measure of the alpha-amylase content and also of the liquefying power of the preparation at zero time under the specified conditions. The nature of the liquefon unit and its applicability to alpha-amylase have been previously discussed (*4*). In addition to the new method of calculation the authors have made significant changes in experimental procedure which are outlined below.

Equipment

The equipment is essentially that used in the original method (*6*), but with the following changes: It is very important to select precipitating jars of uniform dimensions, since the stirring efficiency depends on the size of the jar. A pipet should be chosen which has a time of drainage from mark to mark of 165 to 190 seconds at 21° C. for the specified glycerol solution. A constant-temperature bath should be used and the water pumped through the jacket of the pipet.

The equipment could be easily modified, but it is always necessary to use reproducible technic.

Preparation of Standard Starch Paste

In making up the starch paste it is important to add the starch as soon as the water boils, in order to avoid any considerable loss of water. The first stirring should be for about 1.5 minutes and the second for 2 minutes. In cooling the paste one should use a water bath at about 20° C. Too rapid cooling produces an unstable paste. In the modified method sodium chloride is used to stabilize the enzyme infusions. Accordingly, a satisfactory paste, when mixed with 10 per cent of its weight of water containing 250 mg. of sodium chloride per 100 ml. and stirred for 1 minute, should

give the same outflow time at 21° C., within 10 to 15 seconds, as the glycerol solution specified (*6*).

The time of stirring will vary according to the efficiency of the stirrer, and each operator must adjust his conditions to obtain a standard paste. After stirring with salt solution, a satisfactory paste has an outflow time within 10 to 15

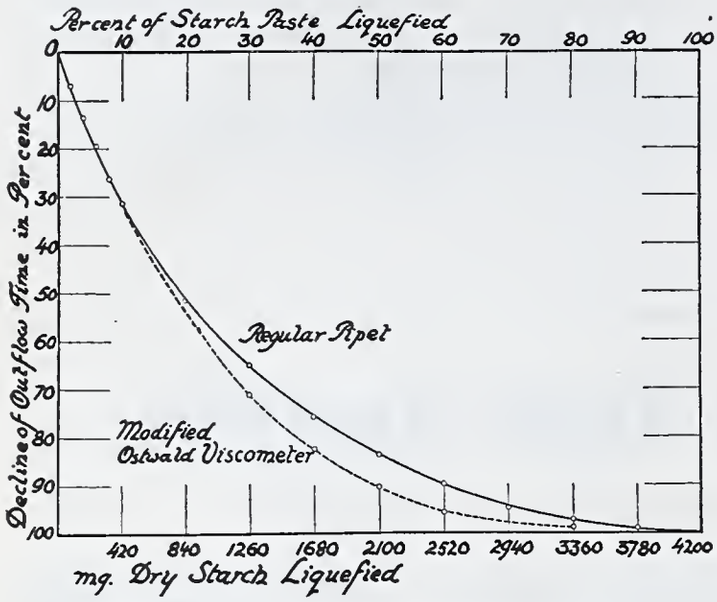

FIGURE 1. STANDARD LIQUEFYING CURVE

seconds of that of the glycerol solution, but for accurate measurements, the initial viscosity of the paste—that is, the viscosity of the paste after stirring with water or enzyme solution—should check the outflow time of the glycerol solution as closely as possible. Accordingly, a paste after stirring with 10 per cent of its weight of water containing 250 mg. of sodium chloride per 100 ml. has a correct initial viscosity if its outflow time checks that of the glycerol solution within 2 seconds. The starch paste before stirring with water is rarely constant enough in viscosity to enable the operator to get the correct initial viscosity at the first stirring, but the correct viscosity is easily attained. If the paste is too viscous after stirring for 1 minute with 10 per cent of dilute sodium chloride solution, it is only necessary to extend the stirring of a second blank a few seconds until a correct initial viscosity is obtained. Similar considerations apply in the case of a paste of low viscosity. The enzyme tests should be stirred for the same length of time that is determined for the blank.

Liquefying Curve

The "liquefying curve" as described in the original publication (*6*) represents the fundamental relation between viscosity and degree of liquefaction of the starch paste. Strictly, each pipet has its characteristic curve, but the authors have found that pipets of widely different outflow times gave essentially the same liquefying curve within 4 to 5 per cent deviation from an average curve. All the liquefying curves determined were smooth from beginning to end, which is not in agreement with the results of Fletcher and Westwood (*1*), who found the liquefying curve to be characterized by a rapid change in slope at about 5 per cent liquefaction. Their results are possibly due to insufficient mixing. The liquefied starch must be gently but thoroughly mixed into the starch paste, particularly when the percentage of liquefied starch is small—below 10 per cent liquefaction. In addition, the pipet must be carefully cleaned and dried before each measurement if the greatest accuracy is to be realized. The authors also checked the liquefying curve by using a modified Ostwald viscometer and found that it was perfectly smooth throughout. Viscometers of the Stormer type were tried, but are unsuitable for this work because of the pronounced disintegrating action of the rotating cup.

Figure 1 shows the relationship between the percentage of starch liquefied and the percentage decline in outflow time for a pipet conforming to the specifications and for the modified Ostwald viscometer. Each point on the standard curve represents the average of sixteen measurements with various pipets and each point on the curve for the modified Ostwald viscometer the average of three measurements. This curve was plotted on large-size cross-section paper and the values of the variables were read from the graph. The data obtained are given in Table I.

TABLE I. PERCENTAGE DECLINE IN VISCOSITY AS A FUNCTION OF THE AMOUNT OF STARCH LIQUEFIED

Viscosity Decline	Starch Liquefied		Viscosity Decline	Starch Liquefied	
%	%	Mg.	%	%	Mg.
1	0.3	13	51	19.4	819
2	0.6	25	52	20.0	848
3	0.9	38	53	20.6	873
4	1.2	51	54	21.3	899
5	1.5	63	55	22.0	929
6	1.8	76	56	22.7	958
7	2.1	89	57	23.4	988
8	2.4	101	58	24.1	1017
9	2.7	114	59	24.8	1047
10	3.0	127	60	25.5	1076
11	3.3	139	61	26.3	1110
12	3.6	152	62	27.1	1144
13	3.9	165	63	27.9	1178
14	4.2	177	64	28.7	1211
15	4.5	190	65	29.6	1249
16	4.8	203	66	30.5	1287
17	5.1	215	67	31.4	1325
18	5.4	228	68	32.2	1363
19	5.7	241	69	33.2	1401
20	6.0	253	70	34.1	1439
21	6.3	266	71	35.1	1482
22	6.6	279	72	36.1	1524
23	6.9	291	73	37.1	1566
24	7.2	304	74	38.2	1612
25	7.5	317	75	39.2	1655
26	7.8	329	76	40.3	1701
27	8.1	342	77	41.5	1752
28	8.5	359	78	42.7	1802
29	8.9	376	79	43.8	1849
30	9.3	393	80	45.1	1904
31	9.7	409	81	46.4	1959
32	10.1	426	82	47.7	2013
33	10.5	443	83	49.1	2073
34	10.9	460	84	50.5	2132
35	11.3	477	85	52.0	2195
36	11.7	494	86	53.5	2258
37	12.1	511	87	55.1	2326
38	12.5	528	88	56.8	2397
39	13.0	549	89	58.5	2469
40	13.5	570	90	60.3	2545
41	14.0	591	91	62.2	2626
42	14.5	612	92	64.2	2710
43	15.0	633	93	66.3	2799
44	15.5	654	94	68.5	2897
45	16.0	675	95	71.1	3001
46	16.5	697	96	74.4	3140
47	17.0	718	97	78.3	3305
48	17.6	743	98	83.2	3512
49	18.2	768	99	89.5	3778
50	18.8	794	100	100	4220

The values of Table I should be applicable to any pipet satisfying the prescribed conditions, with an accuracy of approximately 5 per cent. If greater accuracy is desired it is necessary to determine the characteristic curve of the given pipet. In using the standardized data it is only necessary to determine the final outflow time of the pipet. A fully liquefied starch is prepared according to the directions of the original method and its outflow time is recorded as the final outflow time of the particular pipet used. From the final and the initial outflow times the total range is obtained for a given pipet and the per cent decline in outflow time is calculated for a given measurement. The milligrams of starch liquefied are then read from the table. In order to have available a more complete evaluation of the standard curve, the authors derived the following equation which fits the curve with an accuracy of 1 to 2 per cent over the range from 0.0 to 90.0 per cent decline in outflow time:

TABLE II. STARCH LIQUEFIED

Decline %	Liquefons per 10 cc.	Starch Mg.	Decline %	Liquefons per 10 cc.	Starch Mg.	Decline %	Liquefons per 10 cc.	Starch Mg.	Decline %	Liquefons per 10 cc.	Starch Mg.
50.0	0.691	794	60.0	0.997	1076	70.0	1.601	1439	80.0	2.929	1904
50.2	0.696	799	60.2	1.006	1083	70.2	1.618	1448	80.2	2.971	1915
50.4	0.700	804	60.4	1.015	1090	70.4	1.637	1456	80.4	3.014	1926
50.6	0.705	809	60.6	1.024	1096	70.6	1.656	1465	80.6	3.057	1937
50.8	0.709	814	60.8	1.033	1103	70.8	1.674	1473	80.8	3.102	1948
51.0	0.714	819	61.0	1.043	1110	71.0	1.690	1482	81.0	3.146	1959
51.2	0.719	825	61.2	1.052	1117	71.2	1.709	1490	81.2	3.191	1970
51.4	0.725	831	61.4	1.061	1124	71.4	1.728	1499	81.4	3.236	1981
51.6	0.730	836	61.6	1.071	1130	71.6	1.747	1507	81.6	3.282	1991
51.8	0.735	842	61.8	1.080	1137	71.8	1.766	1516	81.8	3.329	2002
52.0	0.742	848	62.0	1.090	1144	72.0	1.785	1524	82.0	3.375	2013
52.2	0.746	853	62.2	1.100	1151	72.2	1.806	1532	82.2	3.429	2025
52.4	0.751	858	62.4	1.109	1158	72.4	1.826	1541	82.4	3.482	2037
52.6	0.756	863	62.6	1.119	1164	72.6	1.846	1549	82.6	3.537	2049
52.8	0.761	868	62.8	1.129	1171	72.8	1.866	1558	82.8	3.593	2061
53.0	0.766	873	63.0	1.139	1178	73.0	1.887	1566	83.0	3.650	2073
53.2	0.771	878	63.2	1.149	1185	73.2	1.906	1575	83.2	3.705	2085
53.4	0.777	883	63.4	1.159	1191	73.4	1.933	1584	83.4	3.763	2097
53.6	0.782	889	63.6	1.169	1198	73.6	1.956	1594	83.6	3.822	2108
53.8	0.787	894	63.8	1.179	1204	73.8	1.979	1603	83.8	3.880	2120
54.0	0.792	899	64.0	1.189	1211	74.0	2.003	1612	84.0	3.940	2132
54.2	0.799	905	64.2	1.201	1219	74.2	2.026	1621	84.2	4.005	2145
54.4	0.805	911	64.4	1.213	1226	74.4	2.049	1629	84.4	4.071	2157
54.6	0.811	917	64.6	1.225	1234	74.6	2.072	1638	84.6	4.139	2170
54.8	0.817	923	64.8	1.237	1241	74.8	2.095	1646	84.8	4.208	2182
55.0	0.824	929	65.0	1.249	1249	75.0	2.117	1655	85.0	4.277	2195
55.2	0.830	935	65.2	1.261	1257	75.2	2.143	1664	85.2	4.347	2208
55.4	0.836	941	65.4	1.274	1264	75.4	2.169	1673	85.4	4.419	2220
55.6	0.843	946	65.6	1.287	1272	75.6	2.195	1683	85.6	4.493	2233
55.8	0.849	952	65.8	1.300	1279	75.8	2.222	1692	85.8	4.567	2245
56.0	0.856	958	66.0	1.313	1287	76.0	2.248	1701	86.0	4.642	2258
56.2	0.862	964	66.2	1.327	1295	76.2	2.279	1711	86.2	4.725	2272
56.4	0.869	970	66.4	1.339	1302	76.4	2.310	1721	86.4	4.810	2285
56.6	0.876	976	66.6	1.352	1310	76.6	2.341	1732	86.6	4.896	2299
56.8	0.883	982	66.8	1.360	1317	76.8	2.372	1742	86.8	4.982	2312
57.0	0.889	988	67.0	1.379	1325	77.0	2.404	1752	87.0	5.072	2326
57.2	0.896	994	67.2	1.393	1333	77.2	2.435	1762	87.2	5.166	2340
57.4	0.903	1000	67.4	1.407	1340	77.4	2.467	1772	87.4	5.263	2354
57.6	0.910	1005	67.6	1.420	1348	77.6	2.499	1782	87.6	5.361	2369
57.8	0.917	1011	67.8	1.434	1355	77.8	2.532	1792	87.8	5.460	2383
58.0	0.924	1017	68.0	1.446	1363	78.0	2.565	1802	88.0	5.562	2397
58.2	0.931	1023	68.2	1.463	1371	78.2	2.597	1811	88.2	5.668	2411
58.4	0.938	1029	68.4	1.478	1378	78.4	2.630	1821	88.4	5.775	2426
58.6	0.946	1035	68.6	1.493	1386	78.6	2.662	1830	88.6	5.883	2440
58.8	0.953	1041	68.8	1.507	1393	78.8	2.694	1840	88.8	5.996	2455
59.0	0.961	1047	69.0	1.522	1401	79.0	2.727	1849	89.0	6.108	2469
59.2	0.968	1053	69.2	1.538	1409	79.2	2.766	1860	89.2	6.231	2484
59.4	0.975	1059	69.4	1.553	1416	79.4	2.806	1871	89.4	6.355	2499
59.6	0.983	1064	69.6	1.568	1424	79.6	2.847	1882	89.6	6.482	2515
59.8	0.990	1070	69.8	1.584	1431	79.8	2.888	1893	89.8	6.612	2530
									90.0	6.744	2545

$$S = 12.9P - 0.065P^2 + 0.0025P^3$$

where S = milligrams of starch liquefied
P = percentage decline in outflow time

The standardization of the liquefying curve simplifies the method considerably and makes it more available to technological workers. The variable products of reaction produced by different amylase systems have no effect on the general applicability of the liquefying curve. This is shown by the fact that, for a given pipet, solutions having equivalent concentrations of liquefied starch, dextrins, and maltose have outflow times which deviate from one another by not more than 0.5 second. Evidence of this nature has also been submitted by Fletcher and Westwood (*1*).

Use of Sodium Chloride

Jozsa and Gore (*2, 3, 5*) have shown that sodium chloride is effective as a desorption or activating agent and that it tends to stabilize enzyme infusions. Accordingly, the authors have used sufficient sodium chloride in preparing their infusions to make a concentration of 25 mg. per 10 ml. of infusion. In addition to its effect on the enzyme, sodium chloride decreases the viscosity of the starch paste. This effect makes necessary the use of sodium chloride in the blank determination.

Procedure

The actual determination should be carried out as follows:

The 150-gram sample of starch paste is cooled to about 19.5° C., so that after stirring in the enzyme infusion or the sodium chloride solution, the temperature of the stirred paste is 21° ± 0.2° C. The degree of precooling will vary with the stirrer and surroundings, but in any case the paste after stirring should be at 21° C. The correct time of stirring for the proper initial outflow time is determined by running one or more blanks. Using this correct time, 15 ml. of enzyme infusion are stirred into 150 grams of paste and the mixture is placed in the bath at 21° C. After 59 minutes the mixture is sucked into the pipet and its outflow time determined. The measurement of the outflow time of the mixture is begun just before the end of the hour reaction period in order to correct for the liquefaction occurring during the measurement. In order to check the stability of the paste, another blank should be run on 150 grams of paste which has stood for 1 or 2 hours at 21° C. The outflow time of this check blank should not deviate more than 3 or 4 per cent from the first blank. In pipetting the 15-ml. portions it is necessary to avoid the introduction of traces of saliva. A small cotton plug effectively prevents contamination.

Calculations

From the outflow time of a given mixture the percentage decline is calculated, and from this the amount of starch liquefied is obtained by reference to the table or equation. The enzyme content or activity of the infusion is derived from the amount of liquefied starch by means of the empirical equation:

$$\text{Log}_{10}\ L = (S - 1078)\ (0.000565)$$

where L = liquefons per 10 ml. of infusion
and S = milligrams of starch liquefied in 1 hour

From the concentration of the infusion the number of liquefons per gram of preparation is calculated. The number of liquefons per gram of preparation is an exact measure of the alpha-amylase content and also of the liquefying power at zero time.

An example of the calculation is given below:

	Outflow Time Sec.
Paste stirred with water for 60 seconds	181.5
Additional stirring 10 seconds (trial)	164.5
New sample stirred with water for 65 seconds	171.2
(Outflow time with glycerol solution for this pipet is 170 seconds)	
Initial outflow time	171.2
Final outflow time	56.5
Range	114.7
Outflow time with sample (10 mg. per 10 ml.) after 1 hour at 21° C.	91.8

Decline in outflow time: 171.2 − 91.8 = 79.4 seconds

Per cent decline: $\frac{7940}{114.7} = 69.2$

Mg. of starch liquefied (Table II): 1409

$\text{Log}_{10} L = (S - 1078) \times (0.000565)$
where S = mg. of starch liquefied
L = liquefons per 10 ml.
$\text{Log}_{10} L = 331 \times 0.000565 = 0.1870$
$L = 1.538$

Since 10 mg. of the sample were used and this figure must be related to 1 gram of the sample, the result should be multiplied by 100. The alpha-amylase concentration of the sample is measured by the liquefon content, which is 154 liquefons per gram. Its liquefying power at zero time is 3850 mg. of dry starch per minute. Table II gives a convenient tabulation of data obtained from the liquefon-starch equation for the experimental range of 50 to 90 per cent decline in viscosity.

Preparation of Enzyme Solution

Using barley malt (diastatic or pale), 5 grams of malt are weighed into a 1000-ml. flask, 25 grams of sodium chloride are added, and the flask is filled up to the mark. After standing for 1 hour at room temperature with occasional shaking, it is filtered, rejecting the first 100 ml. of filtrate, 100 ml. of the filtrate are transferred into a 1000-ml. flask (or 50 ml. into a 500-ml. flask), and the flask is filled up to the mark.

In case of diastatic malt sirup 2, 5, 10, or 15 grams should be weighed (according to strength) and 25 grams of sodium chloride added, in the same manner as in the above sample.

Various amounts of different enzyme preparations must be used in order to obtain a liquefaction within 50 to 90 per cent decline in viscosity after 1 hour at 21° C. This range has been chosen as most suitable for accurate measurements. Table III gives the concentration of enzymic materials of various strengths in milligrams per 10 ml. necessary for proper application of the method.

Table III. Enzymic Material Required for Analysis of Different Preparations

Liquefons per Gram	Enzymic Material per 10 Ml. Infusion Mg.
1–3	1000
2–6	500
5–15	200
10–30	100
20–60	50
50–150	20
100–300	10
200–600	5
500–1500	2
1000–3000	1

Acknowledgment

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A Simple and Sensitive Test for *p*-Phenylenediamine

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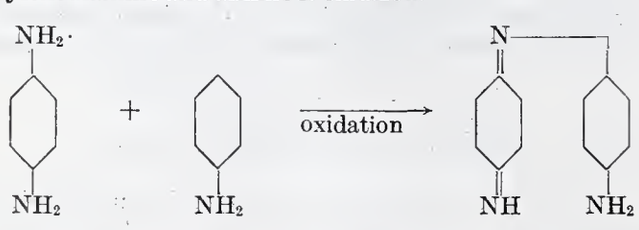
According to Erdmann (*3*), the most sensitive test for *p*-phenylenediamine is the white precipitate of quinone dichlorodiimide produced with sodium hypochlorite, and he recommends diazotation and coupling with β-naphthol disulfonic acid (*2*) for its detection in fur. There are a number of other tests (*1*, *4*), but all have been found unsuitable for detecting the small residual quantities of *p*-phenylenediamine occasionally present in black dyed fur.

The basis of the present test, originally intended to discover small amounts of *p*-phenylenediamine in fur which could not be found by tests commonly found and recommended for this purpose, is the formation of indamine when a mixture of *p*-phenylenediamine and aniline is oxidized.



Treat the test specimen with a small amount of a 3 per cent solution of acetic acid—for example, 6.452 sq. cm. (1 square inch) of fur with 1 to 2 cc. of acid—warm to about 45° C., squeeze the liquid out into a porcelain crucible, add 1 drop of an aniline solution (1 drop of aniline in 50 cc. of water), mix, and add a few crystals of potassium persulfate. The appearance of a blue-green color within about 5 seconds indicates the presence of *p*-phenylenediamine or its derivatives in which the (toxic) *p*-diamine structure has been preserved—for example, *p*-toluenediamine sulfate, which can be considered the salt of a methyl-substituted *p*-phenylenediamine, or dimethyl-*p*-phenylenediamine.

The test is a sensitive one: 0.05 cc. of a 0.00001 per cent aqueous solution (equivalent to 0.0005 mg. or 0.5 gamma of *p*-phenylenediamine) will give a distinct coloration. Interfering substances do not present difficulties. Other amido compounds—so-called oxidation dyes which are employed in pelt dyeing, such as amido phenols, *m*-amido anisol, *o*- and *m*-phenylenediamine—do not respond to the test, but if a trace of *p*-phenylenediamine is present with these substances it will be detected.

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Photometric Investigation of the Ceruleomolybdate Determination of Phosphate in Waters

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WIDESPREAD interest in the occurrence and determination of small quantities of phosphate in water has resulted since Atkins (*1*) first applied the Florentin (*6*) modification of the Denigés ceruleomolybdate method (*4*) to oceanographic work. Although Atkins acknowledged using reagents prepared according to Florentin, he actually used a molybdate reagent with a sulfuric acid concentration greater than recommended in Florentin's original paper. This was probably due to his following the directions given in an abstract of Florentin's paper which specified that sulfuric acid 50 per cent by volume be used in the preparation of the reagent instead of 50 per cent by weight as given by Florentin.

It is well known (*8, 10*) that a certain acidity is necessary to prevent reduction of the molybdate reagent itself by the reducing agent and that the sensitivity of the reagent is dependent upon its acidity and molybdate ratio. After a critical study of the Denigés method, Truog and Meyer (*10*) suggested a molybdate reagent with a reduced acidity and a greater molybdate–sulfuric acid ratio than used by Atkins which in their opinion possessed the optimum sensitivity. Shortly thereafter the Denigés method as used by Atkins was studied spectrophotometrically by Buch (*3*), and by Grippenberg (*8*) who suggested the possibility of using a reagent with a greater molybdate–sulfuric acid ratio to increase the sensitivity of the method. However, the Atkins reagent is the only one that has been used in oceanographic work.

Recently Urbach (*11*) estimated phosphates photometrically in natural waters, using the Bell-Doisy procedure. Unfortunately Urbach's investigations were for a range of phosphate concentrations much greater than normally occur in either the marine or fresh water of this region. Moreover, the original Bell-Doisy method cannot be applied directly to marine work because of the interference of the calcium ions. However, the Briggs modification of the Bell-Doisy method (*2*) does not have this criticism. Another method, first proposed by Fiske and Subbarow (*5*), also gave promise of a possible adaptation to marine work. Recently Giani (*7*) used this latter method photometrically but for approximately the same range of concentrations that Urbach employed. Because of their promise these four procedures were selected for investigation to determine their suitability for the photometric estimation of soluble phosphates, either in the saline or fresh waters of this locality.

Experimental

The phosphate concentrations were estimated by means of the Zeiss Pulfrich gradation photometer. One- and 5-cm. absorption cells were used for the larger phosphate concentrations and a 30-cm. tube for the lesser concentrations. The approximate absorption spectrum of a solution containing 0.005 milligram atom[1] of phosphorus as phosphate per liter was determined for each reagent. The maximum absorption is in the red portion of the spectrum, so the S-72 filter provided with the instrument was used for the remaining measurements. This filter has an effective range of 200 to 250$\mu\mu$. The S-75 filter is less suitable, as the intensity of the transmitted light is insufficient to permit accurate matching of the fields.

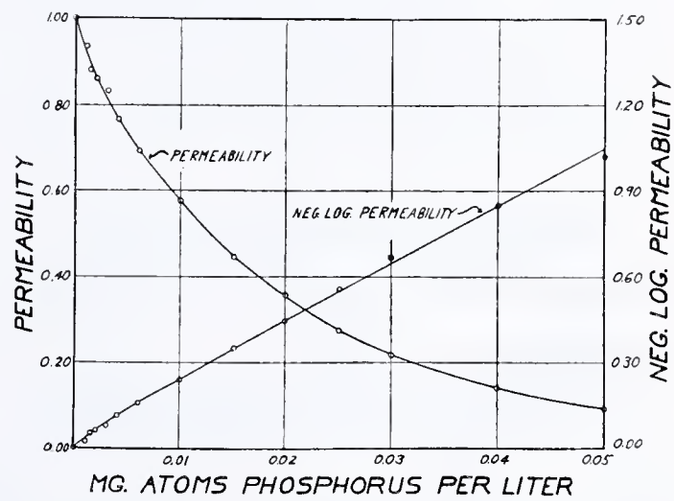

FIGURE 1. PERMEABILITY AND NEGATIVE LOGARITHM OF PERMEABILITY PLOTTED AGAINST PHOSPHATE CONTENT

Atkins reagent in distilled water using a 1-cm. cell. Specific absorption coefficient, 20

The time for the full development of the blue reduction color was determined for each reagent in distilled water and also in sea water. The Bell-Doisy-Briggs and Fiske-Subbarow reagents react very slowly. With these a constant intensity was attained only at the end of 1 and 3 hours, respectively. Using either the Atkins or Truog-Meyer reagents, the maximum intensity occurred 7 minutes after adding the reagents and there was no further change for an hour, after which fading became apparent. Visually fading begins within 10 minutes in marine waters and apparently is due to the formation of a greenish yellow color rather than the diminution of the blue reduction color.

The permeabilities—that is, the fraction of the light transmitted—of the various solutions in the 30-cm. cells were compared with distilled water in a similar cell. With the shorter cells air was used as the reference standard.

Reagents and Procedures

The reagents were prepared from high quality C. P. chemicals according to the following directions.

ATKINS MOLYBDATE REAGENT AND PROCEDURE. To prepare the sulfuric acid–molybdate reagent, 25 grams of ammonium molybdate are dissolved in 250 ml. of distilled water and then added to 750 ml. of sulfuric acid containing 375 ml. of 36 *N* arsenic-free sulfuric acid. The stannous chloride solution is prepared according to the specifications mentioned under the Truog-Meyer procedure.

One milliliter of the molybdate reagent was mixed with each 50 ml. of the sample, followed by one drop of stannous chloride solution. Time for maximum color development was allowed

[1] Milligram atom, mg. at., is defined as the number of milligrams of the element divided by its atomic weight. This term is used in reporting oceanographic data.

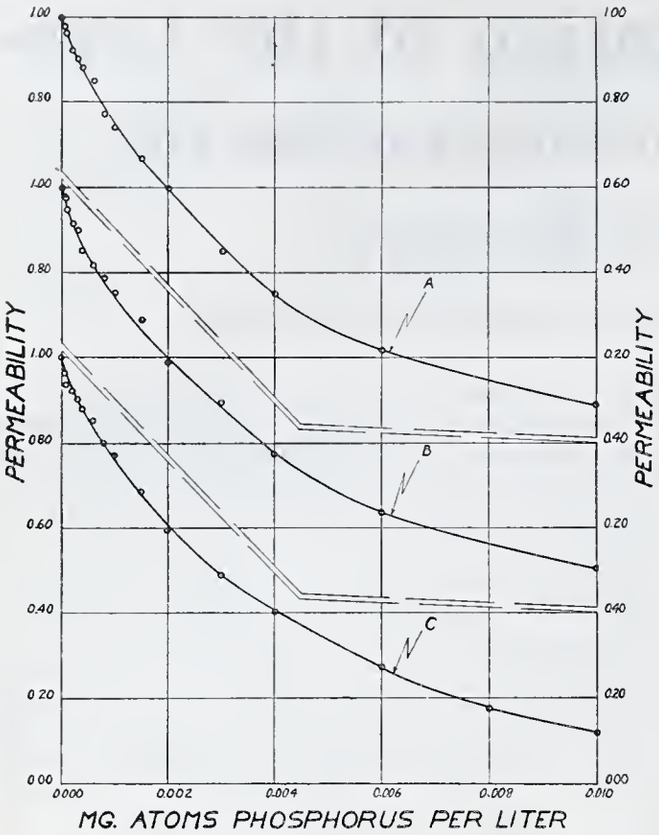

FIGURE 2. PERMEABILITY PLOTTED AGAINST PHOSPHATE CONTENT

5-cm. cell used
A. Atkins reagent in distilled water
B. Atkins reagent in sea water. Cl, 16.5 parts per thousand
C. Truog-Meyer reagent in sea water. Cl, 16.9 parts per thousand

and then the permeability determined. Three ranges of concentrations were studied: 0.000 to 0.050 mg. at. of phosphorus per liter in distilled water using the 1-cm. cell (Figure 1); 0.000 to 0.010 mg. at. of phosphorus per liter in distilled water (Figure 2, *A*, and Figure 3, *A*) and 0.000 to 0.010 mg. at. in sea water of chlorinity 16.5 parts per thousand in the 5-cm. cell (Figure 2, *B*, and Figure 3, *B*); and 0.000 to 0.001 mg. at. in distilled water and in sea water of chlorinity 17.1 parts per thousand using the 30-cm. cell (Figure 4, *E*).

TRUOG-MEYER REAGENTS AND PROCEDURE. The sulfuric acid–molybdate reagent is made to contain 25 grams of ammonium molybdate and 280 ml. of 36 *N* arsenic-free sulfuric acid per liter. To prepare the stannous chloride solution, 25 grams of stannous chloride dihydrate are dissolved in 100 ml. of 12 *N* hydrochloric acid and then diluted to 1 liter. This solution is stored under a layer of oil for preservation as recommended by Truog and Meyer.

Two milliliters of the ammonium molybdate reagent and one drop of stannous chloride were added per 50 ml. of water sample. Two ranges of concentrations were considered: 0.000 to 0.010 mg. at. of phosphorus per liter composed one series (Figure 2, *C*) and 0.000 to 0.001 mg. at. the other (Figure 4, *F*). These concentrations were investigated in both distilled water and sea water, under the same conditions as with the Atkins reagent. The curves for this reagent in distilled water are not included, as they were almost identical with the corresponding curves for the Atkins reagent.

MODIFIED BELL-DOISY-BRIGGS METHOD. In the sulfuric acid–molybdate reagent, 50 grams of ammonium molybdate and 300 ml. of 36 *N* arsenic-free sulfuric acid are present per liter of reagent. One-half gram of hydroquinone is dissolved in 100 ml. of distilled water containing one drop of concentrated sulfuric acid to retard oxidation. A 20 per cent sodium sulfite solution is prepared each day.

To a 50-ml. sample of water were added 2.5 ml. of the acid molybdate reagent, 0.5 ml. of sulfite solution, and 0.5 ml. of hydroquinone in the order named. Since the sensitivity of this reagent was found to be materially less than that of the Atkins or Truog-Meyer reagents, only one range of concentrations was studied. This series extended from 0.000 to 0.010 mg. at. of phosphorus per liter in distilled water and sea water. The photometric comparisons were made in the 30-cm. tubes with distilled water as the reference standard. The curves have not been included because of the unsatisfactory results.

MODIFIED FISKE-SUBBAROW METHOD: To prepare the sulfuric acid–molybdate reagent, 25 grams of ammonium molybdate are dissolved in a liter of dilute sulfuric acid containing 56 ml. of 36 *N* acid. To prepare the aminonaphtholsulfonic acid reagent, 0.5 gram of the dry powder is dissolved in 195 ml. of 15 per cent sodium bisulfite solution, 5 ml. of 20 per cent sodium sulfite are added, stoppered, and shaken until dissolved.

Five milliliters of the molybdate reagent and 2 ml. of the reducing agent were added separately to each 50 ml. of the water sample. Observations were made on series of concentrations ranging from 0.000 to 0.008 mg. at. of phosphorus per liter in distilled water and 0.000 to 0.010 mg. at. of phosphorus in ocean water of chlorinity 16.9 parts per thousand. The 30-cm. absorption cells were used. The curves have not been presented because of the unsatisfactory results.

Discussion of Results

The original Truog-Meyer and Atkins procedures were modified only in the amount of stannous chloride added. At first 3 drops of this solution were used for each 50 ml. of sample. However, this quantity is about thirty-five times the theoretical amount required in sea water and results in the formation of a yellow coloration in addition to the desired blue reduction product. The resulting greenish color makes accurate comparison with the standard solutions impossible by the usual Nessler tube or colorimeter methods of estimation. Reducing the volume of stannous chloride to one drop gives practically no yellow coloration within 10 minutes after adding the reagents and so is advisable in the visual estimation, even though the intensity of the blue color is reduced by 10 per cent as a result. Photometrically the formation of the greenish color does not interfere with the estimation, but the lesser quantity of reducing reagent was used because of the comparison afforded with the visual method.

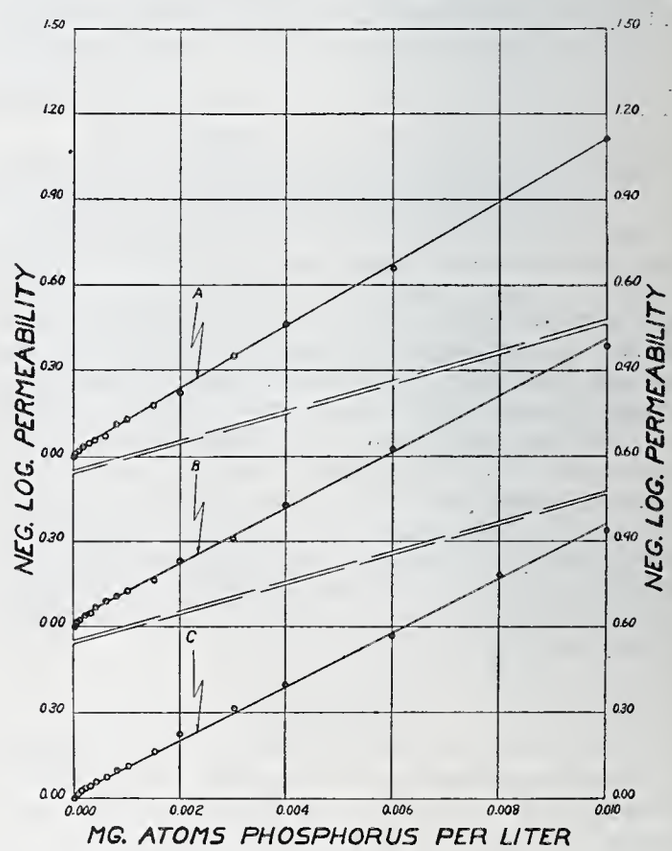

FIGURE 3. NEGATIVE LOGARITHM OF PERMEABILITY PLOTTED AGAINST PHOSPHATE CONCENTRATION

5-cm. cell used
A. Atkins reagent in distilled water. Specific absorption coefficient, 22
B. Atkins reagent in sea water. Specific absorption coefficient, 20
C. Truog-Meyer reagent in sea water. Specific absorption coefficient, 20

When the molybdate reagents as recommended by Bell-Doisy-Briggs and Fiske-Subbarow were tried in sea water, a blue reduction color developed even with no phosphate present. Apparently this was due to reduction of the molybdate reagent itself in a solution whose hydrogen-ion concentration had been materially reduced by the buffer action of the sea water. Doubling the acid concentration of the reagents, as specified above, obviated this difficulty in sea water, yet permitted color development with phosphate in distilled water. Even with the increased acidity an appreciable blank was obtained. Neither the distilled water nor the reagents of Atkins or Truog-Meyer contained phosphate, as the permeability of the blank sample—that is, reagents in distilled water with no phosphate present—was identical with that of only distilled water and molybdate reagent. The sea water, supposedly phosphate-free, was similarly tested and found to contain 0.00005 mg. at. of phosphorus per liter. No correction was necessary for this small amount of phosphate.

Using the various reagents in both sea water and distilled water, standardization curves were constructed by plotting permeability readings, I, against concentration of phosphate. Neither these curves nor the many permeability readings in tabular form have been included in this report, as the authors feel that the standardization curves vary somewhat with conditions and so should be prepared by each experimenter.

The blank determinations, using only the reagents and no phosphate, naturally gave typical photometer readings, I_0, thus making direct comparison of the various standardization curves difficult. To facilitate comparison, the photometer scale readings, I, were divided by the scale reading of the blank determination, I_0, and these values plotted against the phosphate concentrations. This in reality means that the blank solution is now the reference standard and is arbitrarily assigned a permeability of one. It is the curves plotted from these values, I/I_0, that are presented in this article.

In Figure 3 the negative logarithms of the recalculated permeabilities, I/I_0, have been plotted against phosphate concentrations. These curves should be linear if Beer's law is applicable. Examination of Figure 3 shows that at low phosphate concentrations Beer's law does not hold exactly, as the color intensity is proportionally greater than at the higher concentrations. This is true for all four reagents. Grippenberg found not only that a greater degree of reduction occurs in the lower concentrations of phosphate but that the reduction occurs in definite stages as the concentration of stannous chloride is increased. Undoubtedly this observation applies to other reductants, though it was not noted by Urbach, probably because of the higher concentrations of phosphate he was utilizing.

When using the same absorption cell, the slope of the curve, in which the negative logarithm of I/I_0 is plotted against phosphate concentration, is a measure of the sensitivity of the reagent. Moreover the sensitivity is proportional to the specific absorption coefficient. The specific absorption coefficient for the Fiske-Subbarow reagent was 4.4 and for the Bell-Doisy-Briggs reagent 3.3, compared with values of 19 to 23 for the Atkins or Truog-Meyer reagents. From this it may be seen that the two latter reagents are far more sensitive and preferable for the estimation of small quantities of phosphate, such as are found in water. For this reason the methods of Bell-Doisy-Briggs or Fiske-Subbarow are not to be recommended for water analysis except when the phosphate concentration is exceptionally large.

The sensitivity with the Atkins reagent was the greatest in the least concentrated solutions of phosphate, as was indicated by a specific absorption coefficient of 23 (Figure 4, D), compared with 20 (Figure 1) for the higher range of concentrations. This too shows numerically that Beer's law is not applicable. The specific absorption coefficients with the

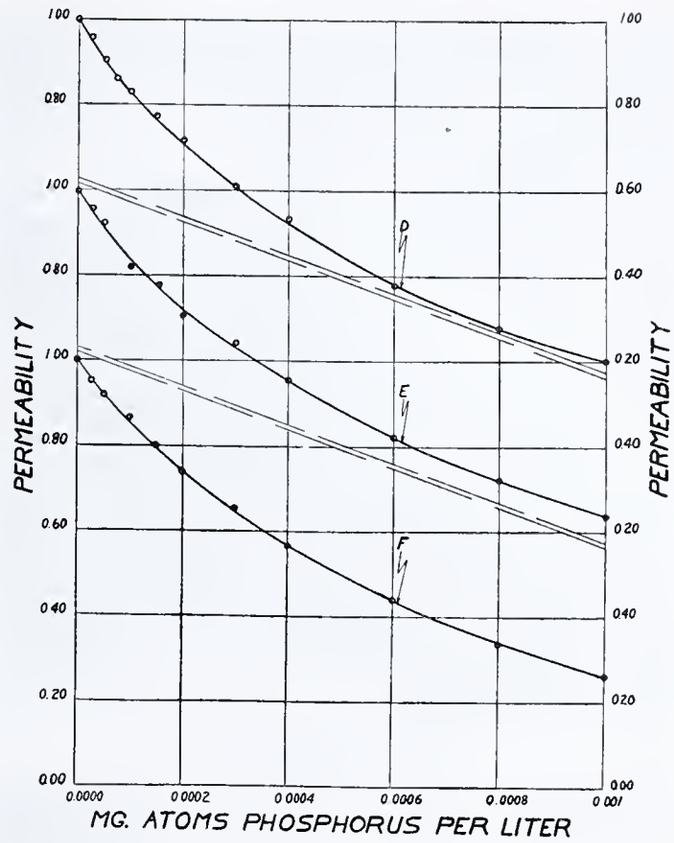

FIGURE 4. PERMEABILITY PLOTTED AGAINST PHOSPHATE CONTENT

30-cm. cell used

D. Atkins reagent in distilled water. Specific absorption coefficient, 23

E. Atkins reagent in sea water. Cl, 17.1 parts per thousand. Specific absorption coefficient, 20

F. Truog-Meyer reagent in sea water. Cl, 16.9 parts per thousand. Specific absorption coefficient, 20

Truog-Meyer reagent in sea water and in distilled water were essentially the same as with the Atkins reagent. This indicates that the sensitivities of the two reagents are approximately the same over this range of phosphate concentrations.

Truog (*9*) has noted that ordinary concentrated sulfuric acid is usually nearer 35 N than 36 N. This fact is not generally appreciated in the preparation of molybdate reagents, so that an Atkins reagent which was thought to be 13.55 N in reality was nearer 13.28 N when prepared and a Truog-Meyer reagent with a specified normality of 10.0 was found to be 9.7. Calibration curves were determined for reagents with these acidities and were found to be identical within the limits of experimental error. This leads to the conclusion that these variations in acidities make no appreciable change in the sensitivities of the reagents.

Grippenberg's work also showed that a reagent having the approximate composition of that of Truog-Meyer possessed an absorption coefficient the same or slightly less than that of Atkins. In general her results showed that increasing molybdate–sulfuric acid ratios, for a given acidity, increases the sensitivity of the reagent, though this was true for only certain portions of the range. She also found that, as a usual thing, an increase in the acidity for a given molybdate content decreases the sensitivity of the reagent. However, for certain acidities and molybdate contents increasing acidity makes little or no difference. That was found to be the case for that range including the Atkins and Truog-Meyer reagents.

The Atkins and Truog-Meyer reagents were found to be slightly less sensitive in sea water than in distilled water. This effect may be expressed numerically by the ratio of the specific absorption coefficients in distilled water and sea water. The average ratio of K_d, for distilled water, to K_s, for sea water, for these two reagents is 1.15 and does not vary

by more than 3 per cent between chlorinities of 12 and 20 parts per thousand. Thus values of phosphate in sea water obtained by comparison with distilled water standards should be multiplied by 1.15 to correct for this salt effect. The Fiske-Subbarow and Bell-Doisy-Briggs reagents were insensitive to this effect.

As a further example of the relative sensitivities of the various reagents photometrically, when using the 30-cm. absorption cell, differences of 0.0001 mg. at. of phosphorus per liter could be detected with the Fiske-Subbarow and Bell-Doisy-Briggs reagents, whereas with the Atkins and Truog-Meyer reagents 0.00001 mg. at. was detectable up to 0.0005 mg. at. of phosphorus per liter. In higher concentrations an estimation may be made with the latter reagents with an accuracy of about 3 per cent. A second advantage is that the development of other colors, such as the yellow coloration in sea water, does not interfere with the estimation of the intensity of the blue. The standard light conditions during estimation is another advantage of the photometric estimation. Moreover, the intensity of the fields of the unknown and standard may be matched with ease by a relatively inexperienced operator, whereas the maximum accuracy is obtainable in matching intensities with Nessler tubes or a colorimeter only after considerable practice.

Conclusions

In the analysis of natural and sea waters containing normal amounts of phosphate, the choice lies between the Atkins and Truog-Meyer procedures. The Bell-Doisy-Briggs and Fiske-Subbarow methods are usable only when extremely large quantities of phosphate are present.

The Truog-Meyer reagent possesses practically the same sensitivity as the Atkins reagent for concentrations of phosphate found in water.

The correction for salt effect for the several reagents has been noted. This effect with either the Fiske-Subbarow and Bell-Doisy-Briggs reagent is negligible. With the Atkins and Truog-Meyer reagents 1.15 times as much color is obtained in a distilled water medium as in sea water.

The yellow color which develops in sea water and which interferes so much with the usual methods of comparison (either using Nessler tubes or a colorimeter) does not influence the photometric estimation.

Using the photometer, a high accuracy is obtainable. With a 30-cm. photometer tube, a difference of 0.00001 mg. at. of phosphorus per liter is readily detectable up to 0.0005 mg. at. In higher ranges of concentrations the estimation may be made with an accuracy of approximately 3 per cent.

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Analysis of Complex Gaseous Mixtures

Using a Combination of the Podbielniak Distillation Column and the Shepherd Apparatus

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IN THE course of some work on the pyrolysis of propane, it was necessary to make quantitative determinations of nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, ethane, propylene, and propane in a mixture which might contain any or all of these components. Since this necessitated modifications of standard procedures, the methods used to overcome some of the difficulties involved may be of interest to others working with these gases.

Preliminary experiments showed that the determination of olefins with sulfuric acid of different strengths (*1*) or with hydriodic acid (*2*, *4*) would not give accurate results. Further, the solubility of most of the other constituents in liquid propane precludes any possibility of the use of fractional condensation as an analytical procedure.

The sample was therefore separated into convenient fractions by distillation in a standard precision low-temperature Podbielniak column fitted with a 2.6-mm. microdistillation tube (*5*). The recommended procedure for introducing the sample was followed. Any components in the sample which were not condensable at the temperature of liquid air and atmospheric pressure were bled off into a 100-cc. gas buret, but the larger part of the low-boiling gases in the sample were held in solution in the liquid propane at this temperature.

For receiving the fractions from the distillation, a special 100-cc. gas buret was used. This buret instead of being fitted with a compensator tube was connected at the bottom through a side tube to an auxiliary leveling tube of the same bore as the buret itself and located parallel to the buret in a water jacket. At the top the auxiliary leveling tube extended considerably above the gas buret and was open to the atmosphere, serving as a manometer to indicate the pressure of the gas in the buret with respect to the atmosphere. At the bottom the gas buret was also connected through a stopcock to a leveling bottle. During the distillation the three-way cock at the top of the gas buret connected this buret to the distillation column so that the auxiliary leveling tube in connection with the buret then served as a manometer to show the distillation pressure. During this time the rate of distillation could be controlled by the opening in the stopcock at the lower end of the gas buret, and by regulating the reflux in the column the mercury in the gas buret and in the auxiliary leveling tube could be kept at the same level.

When it was desired to separate a fraction, or when the buret was full, the three-way stopcock at the top of the buret was closed, the distillation interrupted by cooling, and the volume read. The three-way cock was then opened to a mercury-filled gas sampling tube and the distillate transferred. The capillary connections were filled with mercury both before and after each

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transfer, to insure the removal of all of the distillate and avoid any loss of hydrogen which might occur if a portion of the distillate were allowed to remain in the capillary tube which was connected by rubber tubing.

The first fraction was taken to include some of the ethylene—that is, the cut was made on the ethylene plateau of the distillation curve—and might contain hydrogen, carbon monoxide, nitrogen, methane, and ethylene. It was analyzed by absorption and combustion in the Shepherd apparatus. The next cut was sometimes made between the ethane and propylene plateaus, giving a second fraction which might contain ethylene and ethane. There is a difference in boiling points between ethane and propylene of about 40° C., which should be large enough to give a sharp break on the distillation curve. However, the column holdup is sufficient to introduce considerable error in the estimation of ethane, especially when only small quantities of this component are present. In samples where the ethane content was low, a measured volume of ethane was added to the sample in the column. This gave an ethane plateau upon which a cut could be made for an ethylene-ethane fraction and an ethane-propylene fraction. In the latter case, if sufficient time was allowed for refluxing, some of the propylene could be separated from the propane; and, if the distillation was interrupted after only a few cubic centimeters of the propylene had distilled, the ethane holdup could be minimized without undue contamination of the ethane-propylene fraction with propane. The last fraction contained the remainder of the propylene, the propane, and any higher homologs.

In samples where sufficient ethane was known to be present, no ethane was added. The first fraction was taken as described, the second was made on the break between the ethane and propylene, and the third was made to include about 50 cc. of propane. This third cut was further analyzed by absorption of the propylene and combustion of the ethane and propane remaining. Propylene and propane boil so closely together that a satisfactory separation could not be made by distillation alone; hence these gases were distilled off together as one fraction and their relative amounts determined by absorption of the propylene. The quantity of gas used for a distillation varied between 800 and 1000 cc.

Analysis of Fractions

The fractions obtained from the distillation were analyzed with a Shepherd gas-analysis apparatus according to the principles outlined by Shepherd (*6*). On account of the accuracy of measurement of gas volumes with this apparatus it was desirable to use it for the olefin absorptions as well as for the combustion analysis. Preliminary experiments showed that the solubility of paraffin gases in oleum did not permit the use of this reagent in the accurate determination of olefin gases. In the use of bromine water for the determination of olefins there are several difficulties:

1. If the gas contains a high percentage of unsaturates, it is difficult on account of the slow diffusion of bromine vapors to get these sufficiently mixed with the gas to react completely with the olefins present.
2. When mercury is used as the confining liquid in the gas buret it is necessary to avoid contact of bromine fumes with the mercury.
3. When the percentage of paraffins in the sample is high, the solubility of these gases in bromine water is sufficiently great to introduce serious errors in the determination of small amounts of olefins.
4. When excess bromine vapors are removed after reaction with olefins by absorption in sodium or potassium hydroxide, the evolution of oxygen by decomposition of the hypobromite formed must be avoided.

These difficulties were overcome as follows: Instead of the bromine water ordinarily used in gas analysis, a solution saturated with both sodium chloride and bromine was used as the absorbing medium. This solution, it was shown by test, dissolves paraffins to a negligible extent. It was placed in the extra pipet provided on the Shepherd apparatus for the storage of nitrogen. Following this bromine pipet an additional pipet of the surface-absorption type was added which contained 25 per cent sodium hydroxide solution for the removal of bromine fumes.

As the result of considerable preliminary work, the following procedure for the olefin absorption was adopted:

After absorption of the carbon dioxide and measurement of the residue, the gas was passed to the bromine pipet. If the percentage of olefins was high, all of the mixture was bubbled through the solution. If low, part of the gas was bubbled through the solution and the remainder passed into the excess bromine fumes, the object being to expose as small a quantity of the gas as possible to the solution and at the same time to insure excess bromine in the gas. The brominated gas was next drawn into the sodium hydroxide pipet by suction applied to a rubber tube connected to the reservoir side. It was then forced through the manifold to the potassium hydroxide pipet used for the carbon dioxide absorption, and passed back and forth between these pipets until all traces of bromine were absorbed. This procedure was necessary to remove the bromine from the capillary connection between the bromine and sodium hydroxide pipets, but the gas was not bubbled through the potassium hydroxide solution and only traces of bromine reached this pipet. From the potassium hydroxide pipet the gas was returned to the buret to flush out the olefin-containing gases in the remainder of the manifold. To remove the last traces of olefins the entire procedure was repeated.

Any error caused by the evolution of oxygen in the sodium hydroxide pipet was minimized by frequent renewal of this reagent.

Those gases which were not absorbed were burned according to the combustion procedure recommended by Shepherd, using analyzed oxygen and a calibrated manifold.

There has been some criticism (*3*) of the so-called "simple arithmetic" calculations necessary for correcting for the capillary dead space in the Shepherd apparatus. However, if these corrections are arranged as a factor by which the volumes of the combustibles found may be multiplied to place them on the same basis as the constituents removed before combustion, much confusion can be eliminated. Furthermore, by proper arrangement of the terms this factor can be determined with a slide rule to an accuracy far greater than necessary.

This factor may be determined as follows:

Let F = correction factor
S = original sample of gas
S_1 = reading previous to combustion
a = total volume of nitrogen added to sample from the gas space other than the buret
b = volume of gas not subjected to combustion

Then

$$F = \frac{S_1}{S_1 - \left(b - b\,\dfrac{a}{S_1 + a}\right)}$$

$b\,\dfrac{a}{S_1 + a}$ = volume of nitrogen left in the gas space outside of the buret

$b - b\,\dfrac{a}{S_1 + a}$ = volume of combustible gas not burned

The denominator, then, is the volume of the original gas which was subjected to combustion.

The use of this equation may be illustrated by an example:

S_1 =	78.20 cc.	H_2 uncorrected	= 25.27 cc.
a =	3.60 cc.	CH_4 uncorrected	= 35.50 cc.
b =	1.32 cc.	Residue uncorrected	= 17.55 cc.
ab =	4.75 cc.		

$$F = \frac{78.20}{78.20 - \left(1.32 - \dfrac{4.75}{3.60 + 78.20}\right)}$$

$$F = \frac{78.20}{76.94} = 1 + \frac{1.26}{76.94} = 1.0164$$

Corrected H_2 = (25.27) (1.0164)
= (25.27) (1) + (25.27) (0.0164) = 25.68 cc.
Corrected CH_4 = (35.50) (1) + (35.50) (0.0164) = 36.08 cc.

The correct volume of nitrogen, it follows, is the final residue minus the volumes added to the combustibles found:

Corrected N_2 = residue − (25.27 + 35.50) (0.0164)
= 17.55 − 0.99 = 16.56 cc.

If this calculation still seems too complicated, a chart or a table may be arranged for a particular apparatus, giving the correction factor for each precombustion reading.

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Determination of Ammonia and of Amide Nitrogen in Plant Tissue

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The ammonia present in plant tissues as ammonium ions—that is, the so-called free or preformed ammonia—has been determined since the time of Boussingault by distillation with magnesium oxide, preferably *in vacuo*. A study of the possibilities of interference from a number of commonly found plant constituents, and of the conditions under which this determination is frequently conducted, has led to the suggestion of a technic that depends upon distillation *in vacuo* with a borax–sodium hydroxide mixture used in conjunction with a phosphate buffer solution. The ammonia is then nesslerized and determined in a Pulfrich spectrophotometer. Under these conditions, interference from other substances is minimal. The new reagent is particularly designed for determinations of ammonia in solutions to which phosphate buffers have been added, as the use of magnesium oxide is then inadmissible; its convenience, however, suggests that it may be generally applied with advantage.

The determination of ammonia is the fundamental analytical operation upon which information regarding the amide content of plant tissues is based. Amides are invariably estimated by determining the increase in ammonia nitrogen after hydrolysis under suitable conditions, and, consequently, the accuracy of the information obtained is entirely dependent upon the accuracy with which the quantity of ammonia already present as ammonium ions is ascertained.

The problem presented by the analysis of plant tissues has much in common with the determination of ammonia in urine. Although urea is seldom present as a constituent of higher plants, several substances which are easily decomposed with the production of ammonia are frequently found in them, notably the amide glutamine; allantoin is not uncommon, and even asparagine, which is almost universally distributed, is not so stable that the possibility of its partial decomposition during the determination of ammonia can be safely overlooked.

No review of the extensive literature on the subject of ammonia and amide nitrogen determinations in plant tissues can be attempted here. The foundations of most of the present-day methods were laid by the distinguished French agricultural chemist Boussingault in 1850 (*2*); he first suggested distillation with magnesium oxide to determine ammonia in the absence of urea, he first employed a current of air through the apparatus to promote a rapid transfer of the ammonia, and he first suggested vacuum distillation if urea were present. Furthermore he experimented, although unsuccessfully, with the idea of aëration of the ammonia, a procedure that has been highly developed by Folin (*7*). Only two fundamentally different ideas have been introduced into the field since that time; of these one—gaseous diffusion of the ammonia from cold alkaline solution to standard acid in an enclosed space—was suggested by Schlössing (*17*) in 1851, was almost immediately applied to the difficult problem of urine analysis by Neubauer (*15*), and has recently been placed on a modern footing by Conway and Byrne (*6*). The other new idea is the use of Permutit to absorb ammonia from faintly acid solution, first suggested by Folin and Bell (*8*) in 1917.

Although the work of Bosshard (*1*), Longi (*14*), Wurster (*24*), Folin (*7*), Castoro (*3*), Folin and Denis (*9*), Vickery and Pucher (*20*), Klein and Tauböck (*11*), and Schlenker (*16*), to mention only a few of the investigators who have dealt directly or indirectly with the problem, has furnished a mass of information regarding methods, and the precautions that must be observed in determining ammonia in plant tissues and in urine, only Bosshard and Castoro have specifically considered the possibility of serious interference from glutamine and suggested means for avoiding it. Bosshard precipitated the ammonia with phosphotungstic acid previous to distillation with magnesium oxide—an inconvenient procedure quite unsuited for microscale work; Castoro distilled *in vacuo* with magnesium oxide, but provided inadequate data in support of this method.

Recent experience in this laboratory has suggested that glutamine may be much more widely distributed in nature than has previously been thought, and the authors have accordingly undertaken the development of a method to determine ammonia that is applicable in the presence of this unstable substance. The fundamental ideas employed are those of Boussingault and, in fact, the apparatus suggested differs only in detail from that used by him; the new features are merely a particular combination of modern technics and equipment together with the use of reagents selected according to physico-chemical principles.

The proposed method involves the distillation of a sample that contains from 0.01 to 4.0 mg. of ammonia nitrogen with a buffered alkaline reagent in a simple vacuum apparatus at 40° C. The ammonia is absorbed in acid, the solution is treated with Nessler reagent, and the color produced is read in a Pulfrich spectrophotometer. The extinction coefficient observed is converted to milligrams of ammonia nitrogen from the calibration curve of the instrument.

Apparatus

The apparatus is shown in Figure 1. It is constructed by sealing standard taper ground-glass joints to a 500-cc. Pyrex ring-neck flask to serve as a still, and to a 28 × 200 mm. Pyrex test tube to serve as combined receiver and condenser. The exact dimensions of the trap and vapor tube are immaterial, but the ones shown are convenient. The condensing device is extremely simple; the receiver is supported in a pint milk bottle furnished with a sponge rubber cushion at the bottom, and filled with cold water; a long water-jacketed condenser has been found unnecessary. The distilling flask is loosely clamped to a stand that likewise carries the water bath, so arranged as to be easily raised to immerse the entire flask with water during a distillation, and lowered at the end to facilitate the substitution of a second identical flask for the next determination. A duplicate receiver is likewise provided. The air inlet tube admits air that has passed through a small wash bottle charged with dilute acid to prevent the advent of ammonia from the laboratory air.

A perfectly serviceable apparatus can be constructed from a 3-neck flask and other parts connected by rubber stoppers. In this case, however, the most careful attention must be paid to the preliminary blank distillations, and to the apparatus blank mentioned below.

Reagents

Phosphate-borate buffer, pH 6.5: a mixture of 750 cc. of 0.1 *M* potassium dihydrogen phosphate (13.6 grams per liter) and 250 cc. of 0.05 *M* borax (19.1 grams per liter).

Borax–sodium hydroxide mixture: 5 grams of borax dissolved in 100 cc. of 0.5 *N* sodium hydroxide. The purest sodium hydroxide free from ammonia must be employed.

Magnesium oxide: 25 grams suspended in 200 cc. of water.

Nessler reagent: according to Koch and McMeekin (*12*); 150 grams of potassium iodide and 112.5 grams of iodine are dissolved in 100 cc. of water and 150 grams of mercury are added; after this is dissolved, the solution is diluted to 1 liter and poured slowly with stirring into 4875 cc. of 10 per cent sodium hydroxide.

Sulfuric acid: 6 *N*, prepared from special grade low in nitrogen.

Sodium hydroxide: 1 *N*, prepared from high grade ammonia-free reagent.

Preparation of Extract from Fresh Plant Tissue

A sample large enough to ensure that it truly represents the material should be selected; the following directions refer to samples of from 200 to 300 grams:

The tissue is cut with scissors into thin slices with care to avoid loss of sap, is pressed down into a beaker and is then covered with ether and allowed to stand until entirely flaccid (20 to 30 minutes). The ether, together with the aqueous fluid that has exuded, is strained through cheese-cloth into a separatory funnel, the aqueous layer is drawn into a 1-liter flask, and the ether is washed twice with 50-cc. portions of water, this being added to the flask. The tissue, folded in cheese-cloth, is enveloped in press cloth and pressed at the hydraulic press, the dry cake is disintegrated by hand, mixed with water, and again pressed, and this process is repeated once more. The extracts, together with rinsings of the cloths and apparatus, are added to the flask and the solution is made to volume. Extracts can be prepared very rapidly in this way, and extraction of all but negligible traces of ammonium salts is complete.

The method is founded upon the observations of Chibnall (*4*), who showed the possibility of practically quantitative expression of the vacuole content of plant tissue cells after

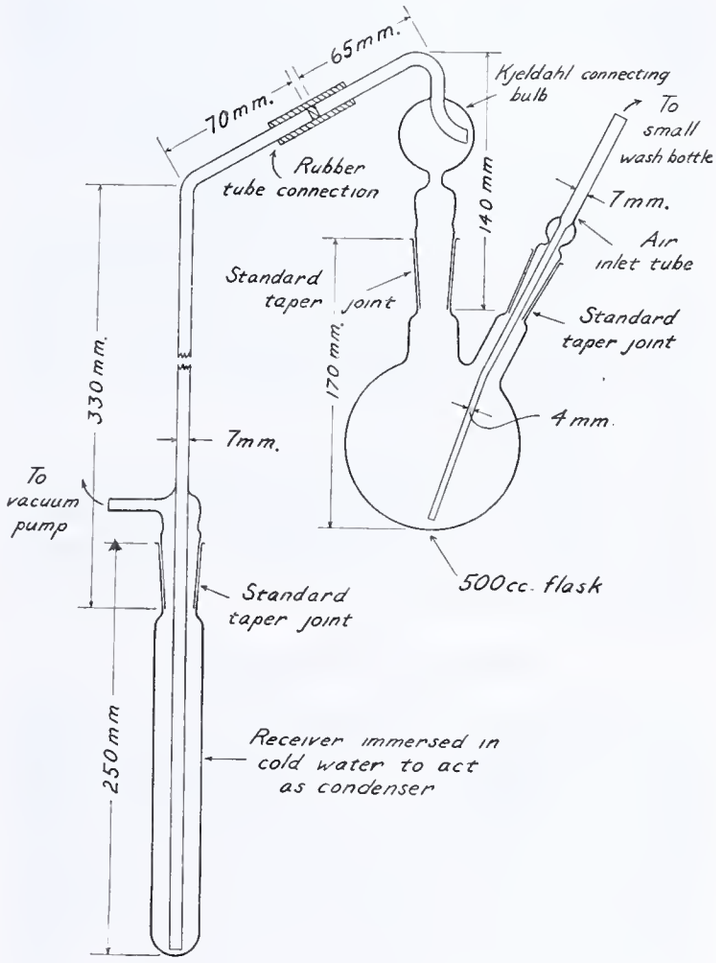

FIGURE 1. DIAGRAM OF APPARATUS

cytolysis with ether. The danger of a significant production of ammonia from the enzymatic decomposition of amides during the relatively brief process is remote, if the results of Grover and Chibnall (*10*) on plant deamidases can be assumed to be generally applicable.

Preparation of Dry Tissue

No entirely satisfactory solution of the problem of drying plant tissues that contain glutamine has come to the authors' attention. If a low temperature is employed, the time required is inconveniently long, and enzymatic processes that produce ammonia may become significant; if too high a temperature is used, hydrolysis of the glutamine takes place. Experiments were conducted in which peat moss, previously washed free from ammonia, was moistened with enough of a dilute solution of glutamine to give a mixture that simulated natural fresh leaf material. Drying could be effected at 68° to 69° C. in 90 minutes with a loss of not more than from 3 to 5 per cent of the amide nitrogen. At 85° to 86° C., a larger quantity of material that required 2.5 hours to dry lost upwards of 20 per cent. The oven employed was fitted with accurate temperature controls, and circulated heated air over the tissue as rapidly as possible without actually disturbing it.

Another factor of great importance is the possibility of loss of ammonia if the reaction of the tissue is appreciably more

alkaline than pH 6.0. The evaporation to half its volume in the oven at 85° C. of a very dilute ammonium sulfate solution buffered at pH 6.95 involved the loss of 14 per cent of the ammonia present. A similar solution at pH 6.03 lost no ammonia under the same conditions.

For the present, then, it is necessary to specify that tissue should be dried at a temperature not exceeding 70° C., and as rapidly as possible. If the natural reaction of the tissue exceeds pH 6, drying without loss of ammonia is probably impossible. In any case, the most careful controls must be instituted in order to obtain information on the probable accuracy of the results. Ammonia determinations on tissue that has been dried at an uncontrolled temperature may have value for the calculation of the residual amide nitrogen, but probably have little physiological significance.

It is sometimes desirable for certain purposes to use water extracts prepared from the previously dried tissue. A method that has proved satisfactory is to transfer 5 grams to a 100-cc. volumetric flask with cold water, dilute to the mark, and shake by machine for several hours. The mixture is then centrifuged, filtered on dry paper if necessary, and 10-cc. aliquots are analyzed. Data that show the accuracy of this method are given below.

A hot-water extract of the dry tissue can also be prepared without undue risk if the glutamine content is not high. To this end, 5 grams of tissue and about 80 cc. of water are rapidly brought to a boil with careful stirring in a beaker, boiled for 3 minutes, cooled, transferred to a 100-cc. flask, made to volume, and centrifuged as before.

Distillation of Ammonia

If dry and finely ground tissue is employed, a sample of from 0.1 to 0.5 gram is thoroughly mixed with 10 cc. of phosphate-borate buffer, and is transferred with the aid of about 20 cc. of water to the distillation flask. If an extract is to be analyzed, a suitable aliquot (usually 25 cc. of fresh tissue extracts prepared as described) together with 10 cc. of buffer, is placed in the flask. The receiver is charged with 3 cc. of 0.1 *N* hydrochloric acid, the joints are lubricated with a little vaseline, and the apparatus is assembled, 3 cc. of sodium hydroxide–borate mixture being added just before inserting the air inlet tube. The apparatus is evacuated, and the air inlet is adjusted to provide a flow of 2 to 3 bubbles per second. The water bath, previously heated to 40° to 42° C., is raised so as to immerse the entire flask, and distillation is allowed to proceed for 15 minutes, the bath being maintained at the same temperature. The bath is lowered, air is admitted through the air inlet, the rubber connection on the vapor tube is opened, and the vacuum pump is disconnected. The vapor tube is rinsed inside and out into the receiver with a few cubic centimeters of water, and the distillate is transferred to a 25 × 200 mm. test tube graduated at 50 cc., or to a 50-cc. flask. Water to make about 35 cc. is added, 5 cc. of Nessler reagent are introduced, and the solution is made to volume and mixed.

Determination of the Ammonia

The light transmission of the nesslerized solution is read in a Zeiss Pulfrich spectrophotometer with light filter S-43. The control solution for the other side of the instrument is prepared by diluting 5 cc. of Nessler reagent to 50 cc. The extinction coefficient is calculated, and the equivalent in milligrams of ammonia nitrogen is obtained from the calibration curve. The final value is corrected for the apparatus blank as described below.

The use of the Pulfrich spectrophotometer to determine ammonia is one of the most valuable applications of this versatile instrument. The details have been worked out by Urbach (*18*, *19*). The authors have confirmed the observation of Wirth and Robinson (*23*) that Nessler reagents prepared by different formulas yield different color values, but find that each type of solution gives highly reproducible results. The same calibration curve has been in use in this laboratory for more than a year with many different samples of Nessler reagent prepared as described. It is necessary for each laboratory to establish the curve for its own reagent and instrument. Known quantities of ammonia nitrogen within the range 0.05 to 2.0 mg. are nesslerized, and read at 50-cc. volume against the control solution. The curve of extinction coefficient plotted against milligrams of ammonia nitrogen should be accurately a straight line between these limits. The curve used in this laboratory is such that extinction coefficient multiplied by 0.286 gives milligrams of ammonia nitrogen.

Accuracy in spectrophotometric work requires great care and considerable experience in reading the instrument. At least five settings should be made that agree within ±1 scale division. Duplicate determinations that disagree by more than ±0.005 mg. of nitrogen should be repeated. Cells should be selected that give readings in the range of 15 to 70 per cent transmission. The upper limit of convenient work is 0.4 mg. of nitrogen in the 50-cc. volume. Higher concentrations necessitate very short cells, and it is usually better to repeat the determination and take aliquots of the distillate.

All determinations are corrected for a small apparatus blank which is redetermined at frequent intervals. The apparatus is charged with 30 to 40 cc. of water, and the distillation is conducted as usual. The nesslerized distillate is read in a 3-cm. cell against the control solution with the control drum set at 50 instead of 100 per cent. The blank is, in the authors' experience, very constant within the limits 0.006 to 0.009 mg. of nitrogen, and can be duplicated within 0.002 mg. A higher blank as a rule indicates that something is wrong, and the source of trouble must be eliminated. The first distillation of the day usually runs high, and it is standard practice to run a blank distillation, after the apparatus has stood unused for some time, and to discard the distillate. The blank for the day is then determined; experience with the method will soon show how frequently a new blank should be run.

When a series of determinations is to be undertaken, the second flask and receiver are prepared during the distillation period, and little time is lost in substituting them.

Table I shows a series of recoveries of 0.5 and 2.5 mg. of ammonia nitrogen. Aliquots of the distillates of the larger quantities were taken before nesslerization, and the data serve to demonstrate that 2.5 mg. of ammonia nitrogen can be quantitatively distilled within the time limit recommended.

Table I. Recovery of Ammonia Nitrogen from Ammonium Sulfate

Taken Mg.	Found Mg.	Recovery %
0.500	0.500	100.0
0.500	0.514	102.8
0.500	0.504	100.8
0.500	0.495	99.0
2.50	2.48	99.2
2.50	2.47	98.7
		Av. 100.1

The average recovery is 100.1 per cent, with an uncertainty in individual cases of slightly less than ±3 per cent. This is the precision to be expected of readings of the Pulfrich spectrophotometer. The method has been applied satisfactorily to the determination of quantities of ammonia ranging from 0.01 to 4.0 mg. The most convenient range is from 0.10 to 0.5 mg.

The application to plant tissues of the present method to determine ammonia involves a consideration of the possibilities of interference from other plant constituents. The most probable interfering substances are glutamine, allantoin, and urea; the stability of asparagine and adenine is also such as to require tests to demonstrate that their presence does not affect the result.

Table II shows in summary form a considerable volume

of data touching on these points. Data to illustrate the necessity for the presence of the buffer solution are included, together with data to show the effect of distillation with magnesium oxide in the absence of buffer solution. It is clear that, if buffer solution is used along with the borax–sodium hydroxide reagent, glutamine interferes to a very slight extent. Urea is rarely found in higher plants, and then only in small proportion; interference from this source is therefore usually negligible. Allantoin, which is more commonly found, is somewhat more stable, and adenine and asparagine show little if any instability under the conditions of the distillation.

Table III shows a series of determinations of the ammonia nitrogen of plant tissues which illustrates the reproducibility of the results, and also serves to show the applicability of the cold-water extraction method as applied to previously dried tissue. The tomato stem tissue is of particular interest, inasmuch as this sample contained 0.565 per cent of glutamine amide nitrogen, or the equivalent of 5.8 per cent of glutamine in the dry material. This sample when distilled *in vacuo* with magnesium oxide, yielded 0.147 per cent of ammonia nitrogen.

Table II. Effect of Distillation on Substances Likely to Be Encountered in Plant Tissue

(With borax–sodium hydroxide mixture or magnesium oxide)

Substance	Ammonia N as Per Cent of Total N: Borax–NaOH	MgO
Glutamine with buffer	0.2 to 0.5	....
Glutamine without buffer	7.8	0.7 to 1.2
Allantoin with and without buffer	0.05 to 0.10	0.15 to 0.25
Urea with and without buffer	0.40	0.40
Adenine with and without buffer	0.01 to 0.03	0.03
Asparagine with buffer	0.00	....
Asparagine without buffer	0.75	0.3 to 0.6

Table III. Determination of Ammonia in Dried Plant Tissue

Sample	Ammonia N Found: Dry tissue	Cold-water extract
	%	%
Tobacco stem press cake E	0.0050	0.0051
	0.0050	....
Tobacco leaf K	0.019	0.020
	0.020	0.021
	0.021	
Tobacco leaf E	0.018	0.021
	0.020	0.022
Tobacco leaf G	0.044	0.044
	0.045	0.045
Tomato stem	0.145	0.145
	0.143	...
	0.145	...

Discussion

The most important novel feature of the present procedure is the use of a borax–sodium hydroxide mixture in conjunction with a phosphate buffer as the alkaline reagent employed to displace the ammonia. The necessity of replacing the time-honored magnesium oxide with a different reagent was revealed in the course of attempts to determine the amide nitrogen of glutamine according to the procedure of Chibnall and Westall (*5*). A detailed study of the conditions under which this determination may be made showed that the amide group is completely hydrolyzed when glutamine is heated at 100° C. for 3 hours in a solution buffered in the range pH 6 to 7 (*22*), but that the distillation of the ammonia produced is frequently far from complete if phosphate buffers are employed. The difficulty was traced to the combined presence of phosphate and magnesium, and can probably be accounted for in terms of the partial precipitation of the ammonia as magnesium ammonium phosphate (*13*). It could usually be avoided if 2 cc. of *N* sodium hydroxide were added along with the 5 cc. of 12.5 per cent magnesium oxide suspension ordinarily employed, but it seemed better for many reasons to avoid magnesium entirely if possible. The borax–sodium hydroxide mixture used together with phosphate buffer solution was found to give the correct conditions for the distillation, and possessed the advantages of being a soluble reagent, and of giving no difficulty with the nesslerization if a little were carried over during the distillation. Magnesium, on the other hand, if carried over, yields a turbid solution useless for quantitative measurements and, should this accident occur, it is necessary to clean the entire apparatus with cleaning acid before it can be used again.

Nevertheless, for many purposes magnesium oxide is equally as good as the borax mixture suggested, and it is frequently employed in this laboratory. The authors avoid its use for tissues that contain notable amounts of glutamine, and it cannot safely be used if phosphate buffers have been employed in connection with glutamine determinations.

Table IV. Recovery of Total Amide Nitrogen of a Mixture of Glutamine and Asparagine

(Figures are milligrams of amide nitrogen)

Asparagine Taken	Glutamine Taken	Amide N Recovered
Mg.	Mg.	Mg.
0.40	0.10	0.488
0.40	0.10	0.508
0.40	0.10	0.506
0.40	0.25	0.644
0.40	0.25	0.642

Table V. Total Amide Nitrogen Content of Several Samples of Dry Plant Tissue[a]

	%
Tobacco leaf B	0.052
	0.053
Tobacco leaf C	0.043
	0.043
Tobacco leaf I	0.098
	0.099
	0.098
Tobacco stem D	0.070
	0.072
	0.070
	0.072
Tobacco stem J	0.050
	0.049
Tomato leaf, ammonia culture	0.448
	0.436
Tomato leaf, nitrate culture	0.087
	0.091
Tomato stem, ammonia culture	0.885
	0.858
Tomato stem, nitrate culture	0.098
	0.100
Beet roots, ammonia culture	0.460
	0.454

[a] The authors are indebted to H. E. Clark for the illustrative data on tomato and beet tissue.

Determination of Amide Nitrogen

Recent studies of the stability of asparagine and of glutamine (*22*) have shown that the conditions for the complete hydrolysis of asparagine advocated by Vickery and Pucher (*21*) are unnecessarily severe. Inasmuch as asparagine is the most stable amide at present known to occur in plants, the total amide nitrogen may be determined under the conditions that have been shown to be adequate for the complete hydrolysis of this substance. These are as follows:

A 5-cc. aliquot of a water extract from the dried tissue prepared as described is mixed with 1 cc. of 6 *N* sulfuric acid in a 25 × 200 mm. test tube which is closed with a stopper that carries a short length of 1-mm. capillary tubing. The tube is heated for 3 hours in a constant-level boiling water bath, the contents are then transferred to the distillation apparatus with 20 cc. of water, 5 cc. of 1 *N* sodium hydroxide are added to neutralize most of the hydrolyzing acid, and 5 cc. of the borax–sodium hydroxide mixture are introduced. The ammonia is determined, and the quan-

tity found is corrected for the apparatus blank, and for the "preformed" ammonia determined directly upon a sample of the dried tissue, not upon the extract. Results that are probably somewhat more trustworthy from the chemical point of view are to be obtained from analyses of extracts from the fresh tissue prepared by the ether cytolysis method. In this case, however, the magnitude of the sampling error may become significant unless the greatest care is exercised.

Table IV shows that the recovery of total amide nitrogen from a mixture of glutamine and asparagine is essentially quantitative under the conditions described, and Table V illustrates the reproducibility of the results on several plant tissues.

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An Automatic Pipet for Rapid Delivery

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IN PERFORMING quantitative experiments it is often advantageous to measure a volume of solution quickly and also to keep it free from some undesirable atmospheric gas. A pipet which does this quickly and efficiently, shown diagrammatically in Figure 1, has been used by the authors to deliver 0.5 *N* sodium hydroxide free from atmospheric carbon dioxide.

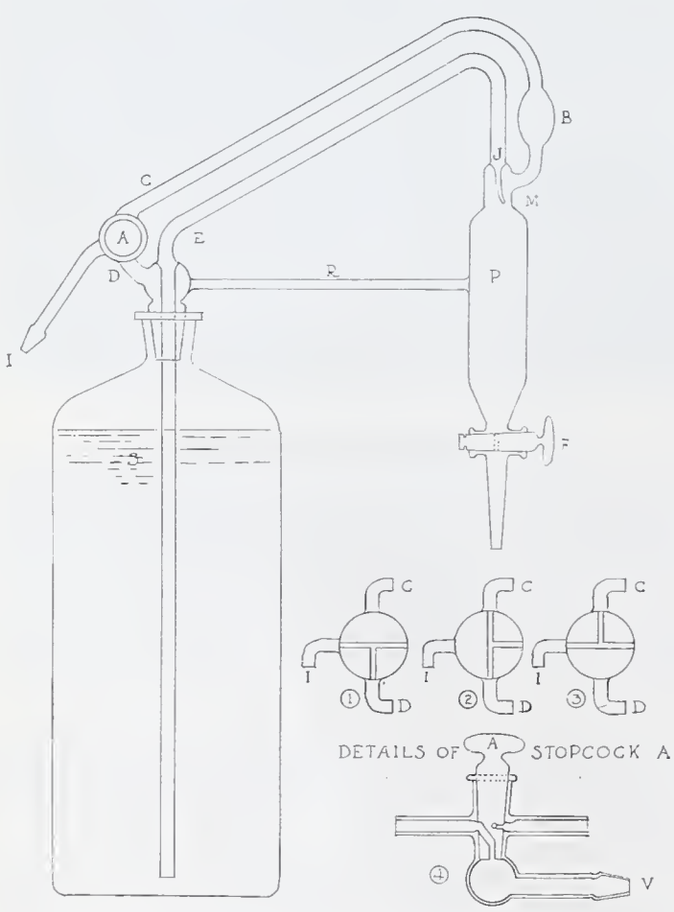

Figure 1. Diagram of Pipet and Stopcock

The simplicity of this apparatus is manifest by the fact that one stopcock, *A*, controls all operations except emptying the pipet. This stopcock plug is a regulation 2-mm. T-bore having special additional drilling. A diagonal hole is drilled from the point just opposite the vertical arm of the T, meeting an axial drilling from the end as shown in 4. The jet, *V*, is not necessary but is very convenient in case the pipet should overflow. The intake, *I*, is attached to a compressed air line, which must be equipped with a Bunsen valve and a scrubber which will remove moisture and carbon dioxide. The pipet may be attached to the solution bottle, *S*, by means of either a rubber stopper or a ground-glass joint. *R* is a reënforcing rod. *B* is an enlarged place in the line to lessen the chances of overflow. The jet, *J*, controls the level of the meniscus line, *M*.

Unless the pipet is small, some additional support is necessary. The authors used a clamp such as that shown by the Fisher Scientific Company, No. 5–778. One end was attached to the neck of the bottle and the other end to the body of the pipet. The use of a bottle as a container for the solution is proposed because it allows the entire set-up to be moved at any time. The specially drilled stopcock is the original and most unique part of the apparatus and any other part of the set-up could easily be changed so as to be more adaptable to the needs of the user.

To start operating the pipet set stopcock *A* as shown in position 1. This admits compressed air through *I* and *D* into the bottle, thus exerting a pressure on *S* and forcing the solution through *E* and *J* into *P*. At the same time, the pressure built up in *P* is released through *B* and *C* and out through *V*. After the level of the liquid in *P* has risen above *M*, the stopcock is turned through a one-fourth turn to position 2. This equalizes the pressure above the liquids in *P* and in the bottle, thus allowing the excess solution to siphon back from *P* into *S* until the liquid level corresponds to *M*. *A* is then turned to position 3 and *F* is opened. The air pressure is thus used to force the solution out quickly. If quick delivery is not required, *A* may be left at position 2 and the pipet will drain freely. When the pipet is not in use, *E* should be closed and *A* set at position 2. This excludes outside air from any part of the apparatus.

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Studies on Turbidity in Sugar Products

III. Transmittancy and Tyndall Beam Intensity of Solutions of Raw Cane Sugars

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IN THE preceding article of this series (*5*), reference was made to a statement by Sauer that the Tyndall beam intensity of colored turbid media can be corrected for absorption by applying a factor based on the optical density of the solution, but, in commenting on this, the writers pointed out that Sauer's procedure could not be used in the case of highly turbid cane-sugar products. Since then an article by Landt and Witte (*2*) on the same subject has appeared. These authors found that with solutions of beet-sugar products filtered through filter paper the results of turbidity determinations, made with the Pulfrich photometer and corrected by means of Sauer's factors, give a reliable measure of the turbidity, and further that there is a close proportionality between the absolute turbidity and the extinction coefficient of the solution.

In view of these findings of Landt and Witte, the writers have reëxamined the experimental results obtained in series C of the previous paper, where mixtures of an unfiltered raw sugar solution, a filtered raw sugar solution, and a filtered white sugar solution, all of 60 Brix density, were investigated, and have calculated the absolute turbidities according to the procedure of Landt and Witte.

The absolute turbidity, t, of the standard block, No. 323, employed by the writers, was reported by Zeiss to equal 0.00282 of the intensity of the incident light, for the green screen L II. The intensity, H, of the four milk-glass disks 1 to 4 was found to be 146.2, 79.0, 24.3, and 18.1, respectively. The cells used were 2.46 mm. in thickness, so that the ratio, D, of the thickness of the standard block to that of the absorption cell was as 16.3 to 2.46 or 6.626. In order to interpolate between the values of the correction factor $f(k)$, given in Table 2 of Landt and Witte, a large graph was prepared based on the relationship: $K = a \log f(k)$.

The results of the calculations, for the three constituent sirups mentioned above, are shown in Table I, which is arranged in the same way as the corresponding Table 4 of Landt and Witte.

TABLE I. CALCULATION OF ABSOLUTE TURBIDITIES ACCORDING TO LANDT AND WITTE

	Unfiltered Raw Sugar Solution	Filtered Raw Sugar Solution	Filtered White Sugar Solution
	5 U, 0 F, 0 W	0 U, 5 F, 0 W	0 U, 0 F, 5 W
Cell thickness, mm.	2.46	2.46	2.46
Filter used	L II	L II	L II
Milk-glass disk, No.	3	2	1
Reading, left drum	45.06	100	100
Reading, right drum	100	40.48	31.50
Relative turbidity	221.9	40.48	31.50
Same, corrected for turbidity of water	216.9	35.5	26.5
A, corrected turbidity/H	8.926	0.449	0.181
Extinction coefficient (for 1.00 cm.)	3.8337	1.8423	0.000
Correction factor, $f(k)$	13.62	3.564	1.000
$A \times f(k)$	121.57	1.600	0.181
Absolute turbidity, $A \times f(k) \times D \times t$	2.2715	0.0299	0.0034
Same, for 1 unit each	0.45430	0.00598	0.00068

It is noted that the asbolute turbidity of the unfiltered raw sugar solution comes out much above 1, which is theoretically impossible, as pointed out by Landt and Witte. This would indicate that the correction factor, $f(k)$, taken from Table 2 of these authors, is very much too high for this type of product, probably because of multiple reflection. The conclusion that the procedure used by Landt and Witte is not applicable to such products is further strengthened by the figures presented in Table II, which gives the absolute turbidities, based on direct calculations, for all the mixtures used in series C and listed in Table V of the preceding article (*5*). For comparison, it shows in the last column the absolute turbidities of the same mixtures, calculated by summing up the component effects of the constituents of each, as determined from the absolute turbidity for one unit of each sirup (last line in Table I).

TABLE II. FOUND AND CALCULATED ABSOLUTE TURBIDITIES OF SIRUP MIXTURES

Mixtures	Absolute Turbidity: According to Landt and Witte	Absolute Turbidity: Calcd. by adding absolute turbidities of constituents
5 U, 0 F, 0 W	2.2715	2.2715
4 U, 1 F, 0 W	1.5814	1.8232
3 U, 2 F, 0 W	0.7718	1.3749
2 U, 3 F, 0 W	0.4212	0.9266
1 U, 4 F, 0 W	0.1764	0.4783
0 U, 5 F, 0 W	0.0299	0.0299
4 U, 0 F, 1 W	1.3983	1.8179
3 U, 1 F, 1 W	0.7231	1.3696
2 U, 2 F, 1 W	0.4132	0.9211
1 U, 3 F, 1 W	0.1775	0.4729
0 U, 4 F, 1 W	0.0289	0.0245
3 U, 0 F, 2 W	0.8451	1.3643
2 U, 1 F, 2 W	0.4088	0.9160
1 U, 2 F, 2 W	0.1759	0.4676
0 U, 3 F, 2 W	0.0282	0.0193
2 U, 0 F, 3 W	0.4498	0.9106
1 U, 1 F, 3 W	0.1737	0.4623
0 U, 2 F, 3 W	0.0154	0.0139
1 U, 0 F, 4 W	0.1512	0.4571
0 U, 1 F, 4 W	0.0117	0.0088
0 U, 0 F, 5 W	0.0034	0.0034

For all mixtures containing unfiltered raw sugar solution, the calculated figures are much higher than the absolute turbidities found, whereas the calculated figures for the mixtures containing only filtered raw sugar and filtered white sugar solution are slightly lower than those found. Furthermore, if the absolute turbidity of one unit of unfiltered raw sugar solution is calculated from the mixtures containing in addition only white filtered sirup, the following figures are found:

Mixture	Value of 1 U
4 U, 0 F, 1 W	$(1.3983 - 0.0007)/4 = 0.3494$
3 U, 0 F, 2 W	$(0.8451 - 0.0014)/3 = 0.2812$
2 U, 0 F, 3 W	$(0.4498 - 0.0020)/2 = 0.2239$
1 U, 0 F, 4 W	$(0.1512 - 0.0027)/1 = 0.1485$

The values for one unit of unfiltered raw sugar solution calculated according to Landt and Witte vary enormously with the concentration, from 0.1485 to 0.4543. Similar discrepant results were obtained also for the absolute turbidities of the Filter-Cel–caramel mixtures discussed in the preceding paper.

The problem of the determination of turbidity in raw cane sugars has therefore been approached by the writers in a different manner, by using the empirical formulas which express the relationship between transmittancy and Tyndall beam intensity on the one hand, and the concentration of coloring matter and turbidity on the other, for the raw sugar employed in the previous investigation. These formulas are:

$$-\log T = C + N$$

$$\log R = (\log a + \log N) - (C \times \log k)$$

where T = transmittancy of a 60 Brix solution of the sugar in a 2.5-mm. cell at a given wave length

R = Tyndall beam intensity, measured under the same conditions as T, and expressed in per cent of that of the standard turbid glass block of the Pulfrich photometer

C = concentration of coloring matter, expressed as $-\log T$

N = concentration of turbidity, also expressed as $-\log T$

The specific absorptive indexes corresponding to the $-\log T$'s have not been calculated, but they are directly proportional to them:

$$-\log t = 5.182 \times (-\log T)$$

For the particular sugar investigated, the following values of the constants $\log a$ and $\log k$ were found:

	Blue, 449 mμ	Green, 529 mμ	Red, 621 mμ
$\log a$	3.13056	3.77551	4.40555
$\log k$	1.42545	1.23280	1.16568

The writers did not have at their disposal a color filter with an effective wave length of 560 mμ, and for this reason the concentration of coloring matter as defined by Peters and Phelps (*3*) ($-\log t$ of the filtered solution at 560) could not be determined. The $-\log t$'s for the three wave lengths available represent therefore merely concentrations of coloring matter based on these wave lengths, but this does not in any way affect the conclusions reached.

In the continuation of this investigation, the transmittancy and Tyndall beam intensity of 60 Brix solutions of 62 other cane raw sugars from many sources have been measured, under the same conditions as specified above. The solutions were prepared by dissolving the sugar in the requisite quantity of water, straining through a 250-mesh bronze sieve to remove coarse particles, and adjusting the density to 60 Brix by refractometer. This solution will be referred to as the unfiltered solution, designated by subscript u. A portion of this solution was filtered through purified Filter-Cel, according to Balch's technic (*1*), and the resulting material is termed the filtered solution, marked by subscript f.

The values of C and N in both unfiltered and filtered solutions were found from the respective figures for T and R, as described in the previous article, by using greatly enlarged graphs similar to the one shown there. The results of the measurements and calculations are shown in Table III, for each of the three color screens.

Coloring Matter

According to Balch, the negative log of the transmittancy of the filtered solution (column headed $-\log T_f$) is a measure of the coloring matter present. All the solutions filtered through Filter-Cel still showed a residual Tyndall beam intensity, R_f, and hence contained measurable turbidity.

This brings up the question of the definition of "coloring matter," or of the dividing line between "turbidity" and "coloring matter" in a medium which, like a raw sugar solution, contains particles of varying sizes, from fairly coarse ones down to those of molecular dimensions. Peters and Phelps have specified that the solutions to be measured for color should show a minimum haze when placed, in a dark room, in the path of a strong beam of light and examined from an angle, and state that no physical constant which quantitatively measures the degree of transparency has so far been utilized. It appears that color determinations cannot be placed on a strictly comparative basis until the degree of transparency is defined. Entirely aside from the subject of selective adsorption of coloring matter by various filtering agents, such as Filter-Cel, asbestos, filter paper, etc., a line should be drawn between what Peters and Phelps term "suitable transparency" and the "lack of it." In the present investigation it is postulated that coloring matter be considered that portion of the dispersed material which gives a Tyndall beam of zero intensity under the experimental conditions used.

Since the Filter-Cel filtrates still showed measurable turbidity, the actual coloring matter contained in them must be smaller in quantity than indicated by the $-\log T$ of the filtrates. In agreement with this, the values for the coloring matter C_f, calculated from $-\log T$ and R of the filtered solution, are smaller than $-\log T_f$. But the question whether the figures for C_f represent the correct concentration of coloring matter as defined above requires a detailed analysis of the data.

Balch concluded from his investigations that specially purified Filter-Cel does not cause selective adsorption of coloring matter, and this was found to be true also for the Filter-Cel used by the writers. This being the case, the quantity of coloring matter actually present in the unfiltered and the filtered solutions of the same raw sugar is necessarily the same—that is, C_u should equal C_f. The tables show that in many cases C_u is the same as C_f, within the limits of error, but in others there are wide divergencies. The explanation for this must be sought in the nature of the turbidity.

Turbidity

As a corollary to the relation between C_u and C_f, the turbidity calculated by subtracting $-\log T_f$ from $-\log T_u$ according to Balch, should be equal to the turbidity difference, $N_u - N_f$, provided, however, that the properties of the dispersed particles, such as average size, distribution of sizes, shape, light transmission, absorption, etc., are the same in different sugars. Conversely, if $-\log T_u - (-\log T_u)$ differs from $N_u - N_f$, the ratio between the two numerically expresses the integrated difference in the properties of the particles. Teorell (*4*) has shown that the $-\log T$ of equal concentrations of an aqueous sol varies with the average size of the particles and the same would apply in the case of a sol in a colored sugar solution. The difference between N_u and N_f, on the other hand, expresses the turbidity in terms of an arbitrary dispersion with fixed particle properties—viz., that existing in the sugar from which the writers' formulas were derived. The ratio between $N_u - N_f$ and $-\log T_u - (-\log T_f)$ is thus characteristic for each individual sugar, and serves as a "quality index" of the particles. Further investigations will have to show what these qualities are, and which of those mentioned above are the more important.

Since $N_u - N_f$ is a measure, in terms of a standard dispersion, of the turbidity filtered out by the Filter-Cel, N_u itself represents the total turbidity in the sugar, in the same terms.

Relation between C_u, C_f, and C

From what has been said, it is now evident why the coloring matter calculated from the transmittancy and Tyndall beam intensity of the unfiltered solution checks with that obtained for the filtered solution only in those cases where the total effect of the properties of the particles causing turbidity is the same as in the standard sugar. It may be inferred that in these same cases C_u, $= C_f$, represents the actual coloring matter, corrected for the residual turbidity in the filtered solution. There are 19 samples among the total of 62 where, under the green screen, C_u equals C_f within ± 3 per cent. For the same 19 samples the C_f values, considered to be equal to C itself within the same limits, are from 0.011 to 0.027 lower than $-\log T_f$. It is interesting to note that for 38 of the other 43 samples the difference between $-\log T_f$ and C_f is within the same range as for the first 19, and that even for the remaining samples it does not exceed 0.031, although in all the 43 the differences between C_u and C_f vary widely. Nevertheless, the conclusion would not be justified that in these 43 cases the actual coloring matter also equals C_f within the experimental error. All that can be said with certainty is that C must be smaller than $-\log T_f$, but the actual difference cannot be derived from the existing data, because the properties of the residual turbidity in

TABLE III. TRANSMITTANCY, TYNDALL BEAM INTENSITY, TURBIDITY, AND COLOR OF RAW SUGARS

No.	Unfiltered Solution				Filtered Solution				$N_u - N_f$	$-\log T_u$ Minus $-\log T_f$	Quality Index
	$-\log T_u$	$\log R_u$	N_u	C_u	$-\log T_f$	$\log R_f$	N_f	C_f			
					A. Blue Filter						
1	1.216	1.842	0.515	0.701	0.774	0.818	0.052	0.722	0.463	0.442	1.048
2	0.373	2.011	0.155	0.218	0.159	1.301	0.023	0.136	0.132	0.214	0.617
3	0.935	1.939	0.388	0.547	0.603	0.867	0.035	0.568	0.353	0.332	1.063
4	1.004	1.884	0.406	0.598	0.694	0.807	0.040	0.654	0.366	0.311	1.177
5	0.611	2.123	0.287	0.324	0.490	1.200	0.050	0.440	0.237	0.122	1.943
6	0.567	2.085	0.253	0.308	0.394	1.269	0.044	0.350	0.209	0.173	1.208
7	0.779	1.962	0.314	0.465	0.546	1.070	0.045	0.501	0.269	0.233	1.155
8	0.742	1.888	0.257	0.485	0.534	0.875	0.029	0.505	0.228	0.209	1.091
9	0.784	2.302	0.448	0.336	0.354	1.103	0.027	0.326	0.421	0.431	0.977
10	0.427	2.093	0.196	0.231	0.238	1.175	0.024	0.214	0.172	0.189	0.910
11	0.608	2.178	0.303	0.305	0.355	1.087	0.027	0.328	0.277	0.253	1.095
12	0.888	2.013	0.390	0.498	0.530	1.077	0.044	0.486	0.346	0.358	0.966
13	1.098	1.779	0.418	0.680	0.766	0.780	0.047	0.719	0.371	0.332	1.117
14	0.462	2.212	0.247	0.215	0.259	1.434	0.041	0.218	0.206	0.203	1.015
15	0.509	2.237	0.276	0.233	0.206	1.448	0.036	0.170	0.240	0.303	0.792
16	0.754	2.119	0.358	0.396	0.455	1.060	0.034	0.421	0.324	0.299	1.084
17	0.580	2.299	0.332	0.248	0.283	1.126	0.023	0.260	0.309	0.297	1.040
18	0.727	1.964	0.283	0.444	0.462	1.019	0.032	0.431	0.251	0.264	0.951
19	0.889	1.951	0.367	0.522	0.593	1.032	0.048	0.546	0.319	0.296	1.078
20	1.218	1.844	0.518	0.700	0.785	0.759	0.050	0.735	0.468	0.433	1.081
21	0.771	1.914	0.292	0.479	0.482	1.144	0.043	0.439	0.249	0.290	0.859
22	1.706	1.745	0.798	0.908	0.970	0.674	0.068	0.902	0.731	0.736	0.993
23	1.520	1.659	0.629	0.891	0.891	0.732	0.061	0.830	0.568	0.629	0.903
24	0.360	2.140	0.182	0.178	0.184	1.459	0.035	0.149	0.147	0.175	0.840
25	0.338	2.292	0.224	0.114	0.108	1.618	0.039	0.070	0.185	0.229	0.808
26	0.356	2.014	0.149	0.207	0.189	1.221	0.022	0.168	0.128	0.166	0.771
27	0.663	2.122	0.312	0.351	0.411	1.115	0.033	0.378	0.279	0.251	1.112
28	0.562	2.372	0.350	0.212	0.268	1.116	0.022	0.246	0.328	0.295	1.112
29	0.660	2.040	0.286	0.374	0.448	1.145	0.040	0.408	0.247	0.212	1.165
30	0.442	2.067	0.209	0.233	0.283	1.115	0.023	0.260	0.186	0.159	1.170
31	1.269	1.805	0.531	0.738	0.806	0.784	0.053	0.753	0.478	0.463	1.032
32	0.736	2.123	0.349	0.387	0.424	0.948	0.024	0.400	0.325	0.312	1.042
33	0.536	2.165	0.265	0.271	0.242	1.047	0.017	0.225	0.248	0.294	0.844
34	1.434	1.731	0.606	0.828	0.900	0.533	0.043	0.857	0.563	0.535	1.062
35	0.351	2.087	0.167	0.184	0.214	1.216	0.023	0.191	0.144	0.138	1.043
36	0.546	1.970	0.209	0.337	0.407	0.992	0.025	0.382	0.184	0.139	1.324
37	0.514	2.134	0.244	0.270	0.283	1.338	0.036	0.247	0.208	0.230	0.904
38	1.132	1.673	0.393	0.739	0.849	0.642	0.045	0.804	0.348	0.283	1.229
39	0.440	2.313	0.269	0.172	0.291	1.447	0.046	0.245	0.223	0.149	1.497
40	0.523	1.879	0.175	0.348	0.404	1.080	0.030	0.374	0.145	0.118	1.229
41	0.706	2.196	0.361	0.345	0.418	1.085	0.032	0.386	0.329	0.289	1.138
42	1.048	1.846	0.415	0.633	0.735	0.899	0.054	0.680	0.361	0.314	1.150
43	1.331	1.938	0.633	0.698	0.744	0.843	0.050	0.694	0.583	0.586	0.995
44	0.566	2.190	0.288	0.278	0.335	1.129	0.027	0.307	0.261	0.232	1.125
45	0.584	2.288	0.330	0.254	0.291	1.301	0.035	0.257	0.296	0.293	1.010
46	0.553	1.857	0.180	0.373	0.405	1.121	0.033	0.372	0.147	0.147	1.000
47	0.500	2.132	0.238	0.262	0.284	1.123	0.023	0.261	0.215	0.215	1.000
48	0.659	2.393	0.412	0.247	0.332	1.247	0.035	0.297	0.377	0.327	1.153
49	0.694	2.018	0.291	0.403	0.463	1.080	0.036	0.427	0.255	0.230	1.109
50	0.429	2.003	0.172	0.257	0.315	1.191	0.029	0.286	0.143	0.114	1.254
51	1.009	1.730	0.350	0.659	0.719	0.819	0.044	0.675	0.306	0.290	1.055
52	0.734	2.401	0.459	0.275	0.288	1.330	0.036	0.251	0.423	0.446	0.948
53	0.568	2.148	0.274	0.294	0.252	1.233	0.027	0.225	0.247	0.316	0.782
54	0.621	2.290	0.351	0.270	0.324	1.386	0.045	0.279	0.306	0.298	1.027
55	0.783	2.226	0.416	0.367	0.381	1.179	0.035	0.346	0.381	0.401	0.950
56	0.387	2.295	0.238	0.149	0.193	1.193	0.020	0.173	0.218	0.194	1.124
57	2.614	0.684	0.921	1.693	1.841	1.778	0.124	1.717	0.797	0.774	1.030
58	0.984	2.004	0.443	0.541	0.630	0.860	0.040	0.590	0.403	0.354	1.138
59	0.694	2.266	0.382	0.312	0.371	1.261	0.040	0.331	0.342	0.323	1.059
60	0.471	2.096	0.215	0.256	0.273	1.197	0.026	0.247	0.189	0.198	0.955
61	0.670	2.205	0.347	0.323	0.408	1.075	0.030	0.377	0.317	0.263	1.205
62	0.821	2.294	0.467	0.354	0.393	0.908	0.020	0.373	0.447	0.427	1.047
					B. Green Filter						
1	0.707	2.811	0.322	0.385	0.347	1.709	0.023	0.324	0.299	0.360	0.831
2	0.251	2.582	0.098	0.153	0.068	1.922	0.017	0.051	0.081	0.183	0.443
3	0.525	2.901	0.273	0.252	0.279	1.679	0.016	0.263	0.257	0.246	1.045
4	0.550	2.785	0.243	0.307	0.322	1.650	0.020	0.302	0.223	0.228	0.978
5	0.331	3.014	0.230	0.101	0.223	1.992	0.030	0.193	0.200	0.108	1.852
6	0.308	2.899	0.186	0.122	0.170	2.004	0.025	0.145	0.161	0.138	1.167
7	0.440	2.794	0.204	0.236	0.244	1.841	0.022	0.221	0.182	0.196	0.929
8	0.379	2.719	0.162	0.218	0.235	1.673	0.015	0.221	0.147	0.144	1.021
9	0.498	3.070	0.323	0.174	0.185	1.726	0.015	0.170	0.308	0.313	0.984
10	0.251	2.719	0.124	0.128	0.095	1.757	0.012	0.082	0.112	0.156	0.718
11	0.355	2.979	0.229	0.126	0.154	1.765	0.015	0.139	0.214	0.201	1.065
12	0.520	2.943	0.287	0.234	0.249	1.828	0.022	0.228	0.265	0.271	0.978
13	0.589	2.858	0.287	0.303	0.343	1.664	0.019	0.324	0.267	0.246	1.085
14	0.280	2.914	0.181	0.099	0.125	2.073	0.027	0.098	0.154	0.155	0.994
15	0.348	2.819	0.178	0.171	0.092	2.049	0.022	0.070	0.156	0.256	0.609
16	0.403	3.003	0.256	0.147	0.193	1.752	0.016	0.177	0.240	0.210	1.143
17	0.361	3.038	0.251	0.110	0.139	2.060	0.026	0.113	0.225	0.222	1.014
18	0.396	2.872	0.212	0.185	0.203	1.802	0.018	0.185	0.194	0.193	1.005
19	0.493	2.869	0.248	0.245	0.274	1.817	0.025	0.249	0.223	0.219	1.018
20	0.692	2.921	0.361	0.330	0.348	1.666	0.020	0.329	0.341	0.343	0.994
21	0.426	2.692	0.170	0.256	0.235	1.927	0.026	0.209	0.144	0.191	0.754
22	0.971	2.974	0.537	0.432	0.445	1.708	0.028	0.417	0.509	0.526	0.968
23	0.841	2.755	0.271	0.570	0.414	1.739	0.027	0.386	0.244	0.427	0.571
24	0.249	2.726	0.126	0.122	0.088	2.096	0.025	0.063	0.101	0.161	0.627
25	0.244	2.839	0.149	0.095	0.069	2.070	0.022	0.046	0.127	0.175	0.726
26	0.216	2.631	0.104	0.112	0.092	1.754	0.012	0.080	0.092	0.124	0.724
27	0.366	2.952	0.225	0.141	0.182	1.821	0.018	0.164	0.207	0.184	1.125
28	0.355	3.083	0.263	0.092	0.127	1.754	0.013	0.114	0.250	0.228	1.096
29	0.355	2.911	0.208	0.147	0.201	1.872	0.021	0.181	0.187	0.154	1.214
30	0.263	2.740	0.133	0.130	0.143	1.791	0.015	0.128	0.118	0.121	0.975
31	0.732	2.881	0.362	0.370	0.378	1.724	0.024	0.353	0.338	0.354	0.955
32	0.427	2.983	0.260	0.167	0.203	1.675	0.014	0.189	0.246	0.224	1.098
33	0.344	2.903	0.202	0.142	0.125	1.680	0.011	0.113	0.191	0.220	0.868
34	0.791	2.939	0.419	0.372	0.402	1.510	0.016	0.386	0.403	0.389	1.036
35	0.181	2.730	0.110	0.071	0.084	1.793	0.013	0.071	0.097	0.097	1.000
36	0.298	2.687	0.142	0.156	0.201	1.732	0.015	0.186	0.127	0.097	1.309
37	0.318	2.731	0.146	0.172	0.162	1.937	0.022	0.140	0.124	0.156	0.795
38	0.602	2.720	0.243	0.359	0.392	1.603	0.019	0.274	0.223	0.210	1.062
39	0.257	2.994	0.196	0.061	0.156	2.115	0.031	0.125	0.165	0.101	1.634
40	0.275	2.597	0.107	0.168	0.189	1.810	0.018	0.172	0.089	0.086	1.035

TABLE III (*Continued*)

No.	Unfiltered Solution $-\log T_u$	$\log R_u$	N_u	C_u	Filtered Solution $-\log T_f$	$\log R_f$	N_f	C_f	$N_u - N_f$	$-\log T_u$ Minus $-\log T_f$	Quality Index
					B. Green Filter (*Continued*)						
41	0.449	2.970	0.267	0.182	0.197	1.749	0.016	0.181	0.251	0.252	0.996
42	0.545	2.785	0.241	0.304	0.325	1.858	0.027	0.298	0.214	0.220	0.973
43	0.783	2.981	0.434	0.349	0.355	1.780	0.026	0.329	0.408	0.428	0.953
44	0.360	2.938	0.219	0.141	0.187	1.775	0.016	0.171	0.203	0.173	1.173
45	0.368	3.013	0.245	0.123	0.167	2.018	0.026	0.141	0.219	0.201	1.090
46	0.312	2.602	0.117	0.195	0.198	1.817	0.018	0.179	0.099	0.115	0.861
47	0.298	2.772	0.151	0.147	0.147	1.737	0.014	0.134	0.137	0.151	0.907
48	0.419	3.119	0.305	0.114	0.159	1.954	0.022	0.136	0.283	0.260	1.088
49	0.391	2.884	0.213	0.178	0.227	1.826	0.020	0.206	0.193	0.164	1.177
50	0.247	2.672	0.114	0.133	0.174	1.823	0.018	0.156	0.096	0.074	1.297
51	0.560	2.702	0.222	0.338	0.347	1.695	0.020	0.326	0.202	0.214	0.944
52	0.473	3.163	0.349	0.124	0.154	1.961	0.022	0.132	0.327	0.319	1.025
53	0.390	2.885	0.212	0.178	0.141	1.795	0.015	0.126	0.197	0.249	0.791
54	0.393	3.016	0.256	0.137	0.181	2.038	0.028	0.153	0.228	0.212	1.075
55	0.503	3.024	0.309	0.193	0.195	1.814	0.018	0.176	0.291	0.308	0.945
56	0.243	2.887	0.162	0.081	0.095	1.788	0.013	0.082	0.149	0.148	1.007
57	1.444	2.216	0.437	1.007	0.841	1.221	0.028	0.813	0.409	0.603	0.678
58	0.605	2.950	0.329	0.276	0.336	1.693	0.020	0.315	0.309	0.270	1.144
59	0.396	3.058	0.273	0.123	0.174	1.959	0.024	0.150	0.249	0.223	1.117
60	0.272	2.756	0.139	0.133	0.139	1.843	0.017	0.123	0.122	0.133	0.917
61	0.401	2.959	0.240	0.161	0.177	1.764	0.016	0.162	0.224	0.224	1.000
62	0.518	3.068	0.333	0.185	0.194	1.589	0.011	0.183	0.322	0.324	0.994
					C. Red Filter						
1	0.401	3.628	0.250	0.151	0.129	2.353	0.012	0.117	0.238	0.272	0.875
2	0.177	3.109	0.068	0.109	0.031	2.315	0.009	0.022	0.059	0.146	0.404
3	0.293	3.565	0.191	0.102	0.108	2.245	0.009	0.099	0.182	0.185	0.984
	0.307	3.557	0.193	0.114	0.130	2.266	0.010	0.120	0.183	0.177	1.034
5	0.176	3.578	0.157	0.019	0.098	2.497	0.016	0.083	0.142	0.078	1.821
6	0.162	3.469	0.127	0.035	0.065	2.428	0.012	0.053	0.115	0.097	1.186
7	0.250	3.503	0.160	0.090	0.116	2.438	0.014	0.102	0.146	0.134	1.090
8	0.203	3.397	0.122	0.081	0.094	2.532	0.017	0.078	0.105	0.109	0.963
9	0.351	3.651	0.239	0.112	0.108	2.259	0.010	0.099	0.230	0.243	0.947
10	0.162	3.313	0.097	0.066	0.041	2.229	0.008	0.034	0.089	0.121	0.736
11	0.216	3.564	0.166	0.050	0.060	2.262	0.009	0.052	0.158	0.156	1.013
12	0.319	3.586	0.206	0.113	0.105	2.390	0.012	0.092	0.194	0.214	0.907
13	0.310	3.572	0.198	0.112	0.120	2.325	0.011	0.109	0.187	0.190	0.984
14	0.156	3.457	0.123	0.033	0.046	2.546	0.014	0.032	0.109	0.111	0.982
15	0.249	3.388	0.131	0.118	0.040	2.468	0.012	0.028	0.119	0.209	0.569
16	0.227	3.618	0.184	0.043	0.070	2.292	0.009	0.061	0.175	0.156	1.122
17	0.236	3.585	0.177	0.059	0.052	2.556	0.016	0.037	0.161	0.183	0.880
18	0.213	3.470	0.140	0.073	0.059	2.312	0.010	0.050	0.131	0.154	0.851
19	0.289	3.524	0.178	0.111	0.125	2.410	0.014	0.112	0.164	0.163	1.006
20	0.382	3.641	0.264	0.118	0.127	2.326	0.011	0.116	0.253	0.255	0.992
21	0.255	3.335	0.122	0.133	0.112	2.515	0.017	0.095	0.105	0.143	0.734
22	0.553	3.790	0.383	0.170	0.177	2.372	0.014	0.163	0.369	0.375	0.984
23	0.477	3.646	0.289	0.188	0.158	2.397	0.014	0.144	0.275	0.319	0.862
24	0.172	3.272	0.092	0.081	0.045	2.547	0.015	0.030	0.077	0.127	0.606
25	0.179	3.403	0.118	0.061	0.042	2.583	0.011	0.031	0.107	0.136	0.787
26	0.139	3.195	0.073	0.065	0.038	2.236	0.007	0.031	0.066	0.101	0.654
27	0.215	3.540	0.149	0.066	0.077	2.331	0.012	0.065	0.137	0.138	0.993
28	0.233	3.626	0.188	0.045	0.057	2.231	0.011	0.047	0.178	0.176	1.011
29	0.206	3.498	0.146	0.060	0.076	2.430	0.013	0.063	0.134	0.130	1.031
30	0.167	3.318	0.099	0.068	0.069	2.278	0.009	0.060	0.090	0.098	0.918
31	0.405	3.626	0.251	0.154	0.153	2.346	0.013	0.140	0.238	0.252	0.944
32	0.251	3.586	0.197	0.054	0.097	2.231	0.009	0.088	0.188	0.154	1.221
33	0.246	3.444	0.143	0.103	0.081	2.182	0.007	0.073	0.136	0.165	0.824
34	0.450	3.724	0.307	0.143	0.146	2.188	0.009	0.137	0.298	0.304	0.980
35	0.108	3.273	0.080	0.028	0.041	2.289	0.009	0.033	0.072	0.067	1.075
36	0.170	3.294	0.095	0.075	0.098	2.261	0.009	0.088	0.086	0.073	1.178
37	0.206	3.323	0.108	0.098	0.091	2.388	0.012	0.079	0.096	0.115	0.835
38	0.325	3.516	0.187	0.138	0.179	2.237	0.011	0.168	0.176	0.146	1.205
39	0.157	3.498	0.133	0.024	0.072	2.581	0.017	0.054	0.116	0.085	1.365
40	0.153	3.216	0.079	0.074	0.086	2.326	0.010	0.076	0.069	0.067	1.030
41	0.310	3.542	0.190	0.120	0.111	2.265	0.010	0.101	0.180	0.199	0.905
42	0.269	3.552	0.180	0.089	0.136	2.454	0.015	0.120	0.165	0.134	1.231
43	0.464	3.676	0.295	0.169	0.149	2.435	0.015	0.133	0.280	0.316	0.886
44	0.250	3.490	0.157	0.093	0.111	2.299	0.010	0.101	0.147	0.139	1.058
45	0.231	3.554	0.168	0.063	0.093	2.442	0.014	0.080	0.155	0.138	1.123
46	0.189	3.211	0.085	0.104	0.106	2.329	0.011	0.095	0.074	0.083	0.892
47	0.211	3.370	0.119	0.092	0.087	2.220	0.008	0.079	0.111	0.124	0.895
48	0.311	3.665	0.228	0.083	0.089	2.391	0.012	0.078	0.216	0.222	0.973
49	0.226	3.481	0.147	0.079	0.115	2.381	0.013	0.102	0.135	0.111	1.216
50	0.152	3.250	0.084	0.068	0.088	2.320	0.010	0.078	0.074	0.069	1.073
51	0.305	3.460	0.166	0.139	0.165	2.328	0.013	0.152	0.153	0.141	1.085
52	0.337	3.720	0.256	0.081	0.095	2.405	0.012	0.083	0.244	0.241	1.012
53	0.285	3.444	0.155	0.130	0.092	2.328	0.010	0.082	0.145	0.193	0.751
54	0.254	3.582	0.182	0.072	0.096	2.483	0.015	0.081	0.167	0.158	1.057
55	0.346	3.606	0.221	0.125	0.112	2.353	0.012	0.101	0.209	0.233	0.897
56	0.159	3.413	0.115	0.044	0.060	2.292	0.009	0.051	0.106	0.099	1.071
57	0.739	3.527	0.362	0.377	0.310	2.195	0.014	0.296	0.348	0.429	0.811
58	0.375	3.631	0.241	0.134	0.160	2.262	0.011	0.149	0.230	0.216	1.065
59	0.246	3.639	0.196	0.050	0.085	2.457	0.014	0.071	0.182	0.162	1.123
60	0.169	3.329	0.101	0.068	0.064	2.368	0.011	0.053	0.090	0.105	0.857
61	0.245	3.543	0.169	0.076	0.108	2.294	0.010	0.098	0.159	0.137	1.161
62	0.339	3.651	0.234	0.105	0 090	2.124	0.007	0.083	0.227	0.249	0.912

the filtered solutions are not known. To solve this question it would be necessary either to devise a filtration method which removes the turbidity completely, or else to ascertain the exact effect of the properties of the residual turbidity in the filtered solution upon its transmittancy and Tyndall beam intensity.

Dispersion Quotient

Teorell also found that for equal concentrations of an aqueous white sol the "dispersion quotient"—i. e., the ratio between $-\log t$ at one wave length and that at another some distance apart from the first—varies with the particle size

of the sol, and that conversely, when the relation between particle size and dispersion quotient has once been determined for a particular substance, the particle size can be arrived at by measuring the dispersion quotient. The question naturally arose whether the dispersion quotient can be made use of to characterize the turbidity in raw sugars.

The dispersion quotient of the filtered solution of a raw sugar is identical with the absorption ratio of Peters and Phelps, designated as Q-ratio when it is based on $-\log t$ at 560 mμ as the reference point, or as Rλ-ratio when it is based on that at another specified wave length, λ. The dispersion quotient of the unfiltered solution, on the other hand, is a function not only of the particle size of the turbid material, but also of the dispersion quotient for both coloring matter and turbidity. In the previous investigation it was further found that even when all the properties of coloring matter and turbidity are exactly the same, the dispersion quotient of the unfiltered solution varies with the ratio between the concentrations of coloring matter and turbidity. It is obvious therefore that the dispersion quotient of the unfiltered solution is a complex function of several variables and cannot be used as a measure of the particle size of the turbid matter.

This leaves for further consideration what may be termed the dispersion quotient for the filterable turbidity—that is, the quotient of $N_u - N_f$ at one wave length, for instance 449 (blue) or 621 mμ (red), divided by that at another, for instance 529 mμ (green). These dispersion quotients are shown in Table IV.

Table IV. Dispersion Quotients for Filterable Turbidity

No.	429 mμ	529 mμ	621 mμ	No.	429 mμ	529 mμ	621 mμ
1	1.549	1	0.796	32	1.321	1	0.764
2	1.630	1	0.728	33	1.298	1	0.712
3	1.406	1	0.708	34	1.397	1	0.739
4	1.641	1	0.821	35	1.485	1	0.742
5	1.185	1	0.710	36	1.449	1	0.677
6	1.298	1	0.714	37	1.677	1	0.774
7	1.522	1	0.802	38	1.554	1	0.786
8	1.551	1	0.714	39	1.351	1	0.703
9	1.367	1	0.747	40	1.629	1	0.775
10	1.536	1	0.795	41	1.311	1	0.717
11	1.294	1	0.738	42	1.687	1	0.771
12	1.306	1	0.732	43	1.429	1	0.686
13	1.390	1	0.700	44	1.286	1	0.724
14	1.338	1	0.708	45	1.352	1	0.708
15	1.538	1	0.763	46	1.485	1	0.747
16	1.350	1	0.729	47	1.569	1	0.810
17	1.373	1	0.716	48	1.332	1	0.763
18	1.294	1	0.675	49	1.321	1	0.699
19	1.430	1	0.735	50	1.490	1	0.771
20	1.372	1	0.742	51	1.515	1	0.757
21	1.729	1	0.729	52	1.294	1	0.746
22	1.436	1	0.725	53	1.254	1	0.736
23	1.436	1	1.127	54	1.342	1	0.732
24	1.455	1	0.762	55	1.309	1	0.718
25	1.457	1	0.843	56	1.463	1	0.711
26	1.391	1	0.717	57	1.949	1	0.851
27	1.348	1	0.662	58	1.304	1	0.744
28	1.312	1	0.712	59	1.373	1	0.731
29	1.321	1	0.717	60	1.549	1	0.738
30	1.576	1	0.763	61	1.415	1	0.710
31	1.414	1	0.704	62	1.388	1	0.705

It is evident that the dispersion quotients shown in Table IV can be a measure of particle size only if the particles do not show selective absorption. Paine and others have found that the colloids removed from sugar products by ultrafiltration are colored, and it is reasonable to suppose that the turbidity absorbs radiation selectively, just as the coloring matter does. An inspection of Table III shows that sugars 18, 35, 56, and 61 have quality indexes of 1.005, 1.000, 1.007, and 1.000, respectively, in the green, and the total effect of the particle properties is therefore the same in all of them, and the same as in the standard sugar. Nevertheless the dispersion quotients of the filterable turbidity vary markedly, being 1.294:1:0.675, 1.485:1:0.742, 1.463:1:0.711, and 1.415:1:0.710, respectively. If the dispersion quotients were the same in these four cases, any deviations from them in other sugars would indicate variations in particle size, but since they are different it must be concluded that the dispersion quotient is affected at least partly by selective absorption by the particles. With the available data it is impossible to decide to what extent either particle size or selective absorption influences the dispersion quotient, but the latter is nevertheless useful further to characterize the nature of the turbidity.

Simplified Procedures

It would be very desirable in routine work to reduce the necessary manipulations, and especially to avoid filtration altogether, if possible. Although the results presented above indicated that the chances for such simplification must be small, this question was further investigated in order to evaluate the limitations of procedures in which the color or the turbidity concentration are derived from the data obtained with the unfiltered solution alone. In this connection many relationships between C_f or $-\log T_f$ under one color screen and values based on the transmittancy and Tyndall beam intensity of the unfiltered solution, under the same and one or both of the other color filters, have been studied. Such correlations do exist, but they are not sufficiently quantitative to be of practical value. It was found, for instance, that the ratio between C_f and C_u in the green, and also that between N_u and $-\log T_u - (-\log T_f)$ in the green decrease with the quotient of C_u in the blue divided by C_u in the green. The formulas giving these relationships are:

$$\frac{C_f}{C_u} = 0.65921 \frac{C_u\,(\text{blue})}{C_u\,(\text{green})} - 0.35896 \qquad (1)$$

$$\frac{N_u}{[-\log T_u - (-\log T_f)]} = 0.47851 \frac{C_u\,(\text{blue})}{C_u\,(\text{green})} + 0.07571 \qquad (2)$$

These formulas make it possible to calculate either C_f or T_f in the green from T_u and R_u in the blue and green, but the precision is low, as shown by the following figures:

	I	II
Mean error, per cent	±11.3	±11.8
Maximum error, per cent	+73.6	+62.2
	−28.1	−25.3
No. of cases within ± 5%	19	13
10%	36	31
15%	45	45
20%	53	57
25%	56	58
30%	58	59
35%	61	60
40%	61	61
65%	61	62
75%	62	..

Similar results were found for the relation between the ratio of C_f to C_u in the green, and the dispersion quotient for $-\log T_u$ in the red and green.

Statistical analyses of all the data were also prepared, but the results were no better. In these analyses the value of $-\log T_u - (-\log T_f)$ was used as the criterion. Formulas 3, 4, 5, and 6, in which (b), (g), and (r) denote the blue, green, and red screens, respectively, are given as examples of the best correlations found:

$$[-\log T_u - (-\log T_f)]\,(g) = 0.50821\,(-\log T_u)\,(g) + 0.000249\,(-\log T_u)\,(b) - 0.030625\,(-\log T_u)\,(r) - 0.17152 \log R(g) + 0.04199 \log R(b) + 0.09818 \log R\,(r) + 0.0709 \qquad (3)$$

$$[-\log T_u - (-\log T_f)](r) = 1.1958\,(-\log T_u)\,(r) - 0.2955\,(-\log T_u)\,(g) - 0.0637\,R\,(r) - 0.0181 \qquad (4)$$

$$[-\log T_u - (-\log T_f)](r) = 0.7797\,(-\log R_u)\,(r) + 0.4738 \frac{\log R(g)}{\log R(r)} + 0.0619 \frac{\log R(b)}{\log R(r)} - 0.4640 \qquad (5)$$

$$[-\log T_u - (-\log T_f)]\,(r) = 0.9937\,(-\log T_u)\,(r) + 1.0024 \frac{\log R(g)}{\log R(r)} + 0.02132 \frac{\log R(b)}{\log R(r)} - 0.1448 \log R(r) - 0.4245 \qquad (6)$$

The precision attainable by the use of these four formulas is as follows:

	III	IV	V	VI
Mean error, per cent	±19.0	±11.3	±10.5	±11.6
Maximum error, per cent	+85.9	+38.4	+40.1	+48.1
	−29.5	−23.1	−33.4	−22.8
No. of cases within ± 5%	10	17	25	19
10%	19	35	37	32
15%	32	43	44	43
20%	38	51	50	54
25%	49	56	55	58
30%	54	57	60	59
35%	55	60	61	60
40%	56	62	61	61
45%	57	..	62	61
50%	59	..	..	62
70%	60	..	..	..
90%	62	..	..	..

It is interesting to note that the precision of the turbidity for the red is somewhat better than that for the green. This is probably due to the fact that the slope of the spectral curves is much smaller at the red than at the blue end.

Summary and Conclusions

The formulas developed in the previous paper (*5*), for calculating the concentration of coloring matter and turbidity in a certain raw sugar from the transmittancy and Tyndall beam intensity of its solution, have been applied to 62 other raw sugars. It has been found that the results obtained by this method check with those of Balch's method only in those cases where the properties of the particles causing the turbidity are the same as in the standard sugar. Conversely, the discrepancy between the results of the two methods serves to characterize the particle properties. Determinations of the transmittancy and Tyndall beam intensity of unfiltered and filtered solutions of raw sugars make it possible (1) to express the concentration of the filterable turbidity, $N_u - N_f$, and also of the total turbidity, N_u, in terms of an arbitrary standard turbidity particle, whereas the difference between the absorptive indexes of the unfiltered and filtered solutions represents merely an optical measure; (2) to estimate the deviation from standard particle properties by the "quality index"—i. e., the ratio between $N_u - N_f$ and the turbidity according to Balch—at one wave length, preferably in the green; and (3) to characterize the absorption quality of the particles by the ratio between $N_u - N_f$ at one wave length and that at another wave length. Value 1 above is analogous to Peters and Phelps' characterization of color concentration by the $-\log t$ at a specified wave length; values 2 and 3 correspond to the characterization of the quality of the coloring matter by the Q or R ratios. It is of course fully realized that neither the color nor the turbidity problem in sugar products can be completely solved without further fundamental knowledge of the chemical and physical properties of the constituent dispersoids present as turbidity or coloring matter, and the procedure outlined in this paper is presented merely as a step in that direction.

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An Emergency Stopper for Nitric Acid Bottles

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REQUIRING a stopper for a bottle containing 98 per cent nitric acid, the author at a venture tried using a cork covered with four thicknesses of ordinary aluminum foil, thinking it would serve for a short time at least until the acid could be transferred. After a few days, it was found that the device was in perfect condition, there being practically no corrosion of the aluminum, and the cork was thoroughly sound. Moreover, it was superior to a glass stopper, since it was air-tight, allowing no leakage of fumes which sometimes occurs with glass-stoppered bottles containing fuming nitric acid.

In order to determine the efficacy of this method in the case of weaker acid as well, a bottle holding 80 per cent acid was closed with a stopper made in the same way as the original one, four thicknesses of foil over cork, and set away with the first bottle. After six months' storage at temperatures ranging from 60° to 80° F., both stoppers were in satisfactory condition. The aluminum in the bottle containing the 98 per cent acid was bright and completely intact, although it was removed several times to withdraw acid. There was some corrosion around the upper part of the stopper, where it did not extend into the bottle, due probably to the action of diluted acid. The foil in the other bottle, containing 80 per cent acid, was dulled somewhat on its inner surface, and was corroded around the circumference, where it was in contact with the glass and remained wetted with the acid. No acid had penetrated to the cork in either case.

This suggests that ordinary bottles with aluminum-covered corks may satisfactorily replace the more expensive glass-stoppered bottles for storing commercial fuming nitric acid. The foil from certain types of candy is easily available and is satisfactory, although a foil having a somewhat greater thickness is preferable. At least four thicknesses of the thinner material should be used. At intervals, the foil may be replaced if it shows corrosion.

The corrosion of aluminum by nitric acid is less the stronger the acid. Dilute acid attacks aluminum rather easily, so it is advised that the stopper be not used for acid weaker than 80 per cent, although it will serve for a short time. Eighty per cent acid in direct contact with aluminum penetrates the metal at the rate of about 0.006 inch per year, while 95 per cent acid penetrates about 0.0025 inch per year (*1*). The slight corrosion of aluminum in contact with the vapor of nitric acid from mixtures containing up to 20 per cent or more water is probably due to a relatively low water concentration in the vapor. Mixed nitrating acid could be stored in bottles stoppered with aluminum without trouble, since the vapors from such acid consist of nearly anhydrous nitric acid, even if the water concentration in the mixture is as high as 25 per cent.

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Determination of Arsenic in Coal

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THE arsenic content of coal has received very little attention in the United States, and few of the procedures for the determination of arsenic in various materials are suited to the analysis of coal. The Bureau of Mines therefore undertook to develop a specific method for the determination of arsenic in coal.

It seemed desirable to titrate the arsenic with some standard solution whose arsenic equivalent could be determined easily, rather than to depend on stains or mirrors that require considerable preliminary standardization before determinations on unknown samples can be made. As the arsenic content of coal is small, the usual titration methods applied to ores containing large amounts of arsenic would not be applicable without considerable modification. However, the method of Archbutt and Jackson (*1*) for the determination of arsenic in coke appeared to be well suited to the analysis of coal.

Method of Archbutt and Jackson

Fifty grams of coke are digested with 100 cc. of hot concentrated nitric acid for at least 2 hours to extract the arsenic. Coal reacts so violently with nitric acid that the acid must be added in small portions and heated cautiously. The mixture is diluted and filtered and the residue discarded. The filtrate is evaporated to dryness, taken up with water and sulfuric acid, and evaporated to sulfuric acid fumes to drive off the nitric acid. The residue is then taken up with water and repeatedly evaporated to sulfuric acid fumes to remove the last traces of nitric acid.

The solution is placed in a distilling flask with ferrous sulfate and sodium chloride and the arsenic distilled off as arsenous chloride. The arsenous chloride and hydrogen chloride are caught in a small volume of water to which zinc sulfide is added to precipitate the arsenic as arsenous sulfide. The bright-yellow precipitate is a good qualitative test for the presence of arsenic. It is seen more easily if hydrogen sulfide is used instead of zinc sulfide, but the zinc sulfide takes less time to precipitate the arsenic completely. This precipitate is filtered off and dissolved by boiling in water. The resulting solution is concentrated, cooled, and titrated with 0.01 *N* iodine.

The Archbutt and Jackson method is accurate to within 0.0005 per cent of arsenous oxide. This is satisfactory for high-arsenic coals, but virtually all the American coals investigated contained less than 0.002 per cent of arsenous oxide, for which a more sensitive method was necessary.

Method Based on Gutzeit Test

The most accurate methods for estimating extremely small amounts of arsenic are the Gutzeit and the Marsh tests, both depending on the liberation of the arsenic as arsine. Of these the Gutzeit seems to be more practicable for use in the average chemical laboratory. It can easily detect 0.000001 gram of arsenous oxide, as this amount will produce a stain 0.3 cm. (0.125 inch) long.

The methods of decomposing and preparing samples for the Gutzeit test are numerous, and several of those recommended for coal have been tested. One is similar to that used by Archbutt and Jackson—the sample of finely powdered coal is digested with concentrated nitric acid and the nitric acid expelled by fuming with sulfuric acid.

In other methods the coal is digested with both nitric and sulfuric acids, but in all of them the nitric acid is eliminated by fuming with sulfuric acid. It is assumed that virtually no arsenic is lost during this fuming process; however, the results of a number of the bureau's experiments indicate that this assumption is incorrect. The amount lost would be of little consequence were it not for the fact that the arsenic content of coal is usually a few ten-thousandths of 1 per cent. It seemed desirable, therefore, to eliminate the use of nitric acid and avoid fuming.

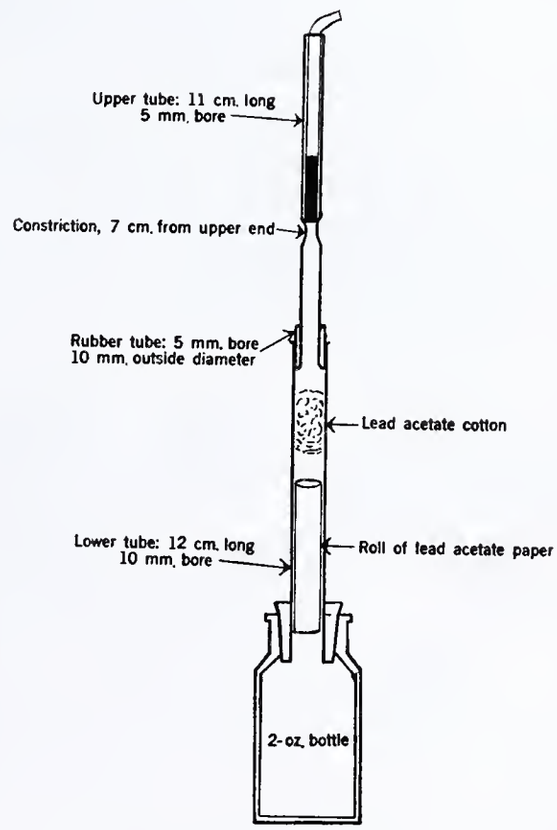

FIGURE 1. APPARATUS FOR GUTZEIT TEST

Nitric acid is also objectionable because of its noxious fumes and copious foaming, which make treatment of the mixture difficult in any vessel of reasonable size. Even after the coal is filtered off, the filtrate is likely to foam and cause trouble throughout the test. Foaming is especially undesirable in a Gutzeit bottle.

A procedure in which the carbonaceous matter is burned off and foaming thereby eliminated is more practicable. Some investigators have ignited coal with lime, sodium carbonate, or similar substances, relying on these reagents to retain the arsenic during ignition. The ash is then extracted with nitric acid and the nitric acid eliminated by fuming with sulfuric acid. In the method finally adopted in this investigation the residue after ignition was treated direct with sulfuric acid, so that there was no nitric acid to remove.

Method Developed

The procedure developed, although similar to many given in the literature, is an attempt to bring together the best features of all.

APPARATUS. The apparatus used is almost the same as that described by Scott (*2*) but is a little easier to make. To bore a straight hole through a very small rubber stopper is rather difficult, so the two tubes are joined with a small piece of rubber tubing. The constriction in the lower tube is not absolutely necessary and so has been eliminated. Figure 1

Table I. Recovery of Arsenic

Run	1	2	3	4
Coal used, gram	1	1	1	1
As_2O_3 added, per cent	None	None	0.0005	0.0005
As_2O_3 found, per cent	0.0004	0.0004	0.0009	0.0009

Table II. Recovery of Arsenic

Run	1	2	3	4
Coal used, gram	1	1	1	1
As_2O_3 added, per cent	None	None	0.0005	0.0005
As_2O_3 found, per cent	0.0005	0.0005	0.0010	0.0009

shows the apparatus and its dimensions. This apparatus can be made from materials available in almost any chemical laboratory and requires no special knowledge of glass-blowing technic.

The constriction in the small tube is very important, as it concentrates the flow of gas and directs it at the mercuric bromide paper. More important, the extreme lower end of the paper falls into this constriction and is held in the exact center of the tube. If the constriction were not there, even though the paper were perfectly straight the fumes probably would cause it to curl to one side and direct all the gas to that side of the paper, making a long stain on one side and a shorter one on the other.

Test Procedure. The following procedure gave the most consistent results and is recommended as the most reliable:

Weigh out a 1-gram sample of minus 100-mesh coal and mix thoroughly with 0.8 gram of a mixture of 5 parts of sodium carbonate, 3 parts of magnesium oxide, and 1 part of potassium nitrate. Place the sample and mixture in a low porcelain or platinum crucible, set in a cold muffle, and raise the temperature to between 700° and 750° C. in 1 hour. The ignition should be continued about 1.5 hours longer to burn out all the carbon. If the temperature does not exceed 750° C. there will be little trouble with sintering. Remove from muffle, cool, and wet residue with a fine stream of water (2 or 3 cc.), washing down sides of crucible. Add concentrated arsenic-free sulfuric acid drop by drop slowly while stirring until solution is acid to litmus.

Wash the contents of the crucible into the Gutzeit bottle. Add 3.5 cc. of concentrated sulfuric acid and, in order, 2 cc. of ferric ammonium alum and 0.5 cc. of stannous chloride from a graduated pipet. Dilute to approximately 45 cc. with distilled water, stir until thoroughly mixed, and place bottle in pan of water at approximately 25° C. Load the lower tube with a roll of lead acetate paper and lead acetate cotton, connect apparatus, and place mercuric bromide paper in the upper tube. Place two pieces of stick zinc in the bottle and cork immediately with the upper part of the apparatus. After 50 to 60 minutes remove the test paper, dip in melted paraffin, and compare with standards.

Standard Stains. In preparing the standard stains add the arsenic solution, dilute with a little water, add 3 cc. of concentrated sulfuric acid, instead of 3.5 cc. as for the samples, and then add the other reagents as described. Standard stains should be made for 0.000, 0.002, 0.004, 0.006, 0.008, 0.010, 0.013, and 0.017 mg. of arsenic trioxides. The stains should be dipped in melted paraffin, not too hot, for a second and then cooled. They may be mounted on a piece of cardboard and kept in a calcium chloride desiccator in a dark place when not in use. The standard will fade gradually with time, but may be photographed to exact size and the print used in place of the stains. With a little practice the reading can be made as accurately as with standard stains, and the print will last indefinitely. Curves plotted through the tops of the stains can be used in place of a set of standards. The effect of ammonium hydroxide and hydrochloric acid in developing the stain was tested but was not thought to have any practical value.

Discussion of Results

Duplicate determinations by this method checked very well, but failed to prove that no arsenic was lost by volatilization. It seemed reasonable to suppose that any method capable of retaining arsenous oxide added in the form of a standard solution would be likely to hold arsenic in any other form in the coal. A sample of Black Creek coal analyzing 1.56 per cent ash, 0.64 per cent sulfur, and 0.25 per cent iron was selected for the test. As the coal was of high purity, the effect of a large amount of inorganic matter was eliminated. Duplicate determinations were made with and without addition of arsenic. The results are given in Table I, and show that all the arsenic added was obtained and recovered.

The same experiment was repeated with a Montana coal analyzing 11.72 per cent ash, 1.22 per cent sulfur, and 1.02 per cent iron, to see if the results were equally satisfactory where the inorganic matter was relatively high. The results shown in Table II indicate that all the arsenic is retained and that all of it can be recovered by the Gutzeit test.

Table III gives the results of duplicate determinations on a number of coals for fixed and total arsenic by the Gutzeit method and shows how closely the results may be expected to check. Fixed arsenic is the arsenic found in the coal after it has been ashed without anything added to retain the arsenic. Duplicate runs by the method of Archbutt and Jackson are also shown and check the Gutzeit method very well within the limits of their error, which is certainly not greater than 0.0005 per cent.

Table III. Comparison of Duplicate Analyses Obtained by Gutzeit and Archbutt-Jackson Methods

			Method of Analysis		
			Modified Gutzeit		Archbutt and Jackson
Sample	Bed	State	Fixed As_2O_3	Total As_2O_3	Total As_2O_3
			%	%	%
1	Jefferson	Ala.	0.0130	0.0140	0.0143
			0.0120	0.0140	0.0139
2	Black Creek	Ala.	0.0004	0.0004	0.0002
			0.0004	0.0004	0.0002
3	Corona	Ala.	0.0007	0.0007	0.0005
			0.0007	0.0007	0.0005
4	Mary Lee	Ala.	0.0015	0.0015	0.0011
			0.0015	0.0015	0.0011
5	Pittsburgh	Pa.	0.0007	0.0014	0.0009
			0.0010	0.0012	0.0013
6	Alma	W. Va.	0.0005	0.0008	0.0006
			0.0006	0.0007	0.0003
7	No. 6	Ill.	0.0007	0.0013	0.0010
			0.0007	0.0013	0.0011
8	Weir-Pittsburgh	Kans.	0.0007	0.0014	0.0010
			0.0007	0.0014	0.0005
9	Bear Creek	Mont.	0.0004	0.0009	0.0005
			0.0004	0.0009	0.0003
10	No. 3	Iowa	0.0008	0.0020	0.0026
			0.0012	0.0022	0.0023
11	Wadge	Colo.	Trace	0.0001	0.0002
			Trace	0.0001	0.0002
12	No. 9	Ky. (western)	0.0008	0.0015	0.0012
			0.0008	0.0015	0.0012
13	Pittsburgh	W. Va.	0.0006	0.0011	0.0003
			0.0007	0.0009	0.0004
14	Lexington	Mo.	0.0014	0.0016	0.0021
			0.0006	0.0018	0.0020

Table IV. Summary of Analyses in Order of Increasing Arsenic Content[a]

Sample	Bed	State	Fixed As_2O_3	Total As_2O_3	Iron	Sulfur	Ash
			%	%	%	%	%
11	Wadge	Colo.	Trace	0.0001	0.19	0.45	7.29
2	Black Creek	Ala.	0.0004	0.0004	0.25	0.64	1.56
3	Corona	Ala.	0.0007	0.0007	0.91	1.98	8.54
6	Alma	W. Va.	0.0006	0.0008	0.86	1.70	5.62
9	Bear Creek	Mont.	0.0004	0.0009	1.02	1.22	11.72
13	Pittsburgh	W. Va.	0.0007	0.0010	1.23	2.76	7.35
5	Pittsburgh	Pa.	0.0009	0.0013	0.82	1.55	6.37
7	No. 6	Ill.	0.0007	0.0013	2.64	4.47	10.48
8	Weir-Pittsburgh	Kans.	0.0007	0.0014	2.10	3.29	7.28
4	Mary Lee	Ala.	0.0015	0.0015	1.23	1.36	15.12
12	No. 9	Ky. (western)	0.0008	0.0015	2.82	4.44	14.50
14	Lexington	Mo.	0.0010	0.0017	2.95	4.76	19.46
10	No. 3	Iowa	0.0010	0.0021	5.02	7.17	19.12
1	Jefferson	Ala.	0.0130	0.0140	2.37	3.35	6.79

[a] Arsenic determinations by modified Gutzeit method.

Table IV summarizes the analyses of all the samples tested in the order of increasing total arsenic. The arsenic does not increase in direct proportion to iron, sulfur, or ash, although there seems to be a general trend in that direction. However, as shown in Table V, in general the arsenic content increases as the other inorganic constituents increase.

Table V. Average Analyses of Groups Taken from Table IV

Number of Samples Averaged	Total As_2O_3	Iron	Sulfur	Ash
	%	%	%	%
2	0.0003	0.22	0.55	4.43
4	0.0009	1.01	1.92	8.31
4	0.0014	1.70	2.67	9.81
4	0.0048	3.29	4.93	14.97

Good checks in arsenic analyses were obtained with 1-gram samples of minus 100-mesh coal. For the high-arsenic Jefferson coal 0.1-gram samples were used satisfactorily. One cube of arsenopyrite which would just pass the opening in a 100-mesh screen would add 0.001 per cent of arsenous oxide to a 1-gram sample.

However, most of the analyses check within 0.0003 per cent, indicating that the arsenic is probably diffused in extremely fine particles throughout the coaly substance and is not concentrated in particles of arsenopyrite of any appreciable size.

Acknowledgments

The author wishes to acknowledge his indebtedness to A. C. Fieldner, who suggested and directed the course of this investigation; to Alden H. Emery, B. W. Gandrud, and E. P. Barrett for many helpful suggestions; and to H. H. Schrenk for check determinations and careful criticism of the manuscript.

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Volumetric Determinations of Halides

Use of Dichlorofluorescein as an Adsorption Indicator

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ADSORPTION indicators for the argentometric determination of halides were suggested by Fajans and his collaborators (*3*, *4*); and Kolthoff, Lauer, and Sunde (*5*) chose dichlorofluorescein as the most suitable substance for the purpose. They gave the results obtained with dichlorofluorescein in the argentometric titration of chlorides, and indicated that equally satisfactory results could be expected in the titration of bromides and iodides. Their work is mentioned in a recent textbook (*7*) on quantitative analysis, which stresses the value of their method only in the determination of chloride. Osterberg (*8*) used dichlorofluorescein as an adsorption indicator for the estimation of chlorides in the blood, carrying out the titrations in an acetone-water solution. During the past two years dichlorofluorescein has been used in these laboratories in many routine titrations with complete satisfaction. This paper will describe the use of the indicator for the analysis of organic hydrochlorides in alcohol solutions, and will give analytical data concerning the argentometric titration of bromides and iodides.

The chlorine analysis of Diothane (piperidinopropanediol diphenylurethan hydrochloride, *1*, *9*), a new local anesthetic, is an important control test. It is desirable to carry out such analytical work on Diothane with the sample in alcohol solution, and it was found that dichlorofluorescein is as satisfactory an indicator in 75 per cent alcohol solutions as in aqueous solutions. Other organic hydrochlorides prepared in the Merrell research laboratories and some anesthetics on the market have also been analyzed in this way.

Halogen determinations on many inorganic compounds have been carried out with dichlorofluorescein as the indicator; among them may be mentioned ammonium chloride, ammonium bromide, ammonium iodide, sodium chloride, sodium bromide, sodium iodide, calcium bromide, potassium bromide, potassium iodide, mercuric chloride (after previous removal of the mercury), and hydriodic acid. The analyses of these inorganic salts were all carried out in aqueous solution.

Titration of Organic Hydrochlorides

The 0.05 *N* silver nitrate solution used was standardized against dried pure sodium chloride (Mallinckrodt analytical reagent) with the following procedure:

Approximately 0.12 gram of the sodium chloride was weighed and dissolved in 80 cc. of 75 per cent alcohol, 8 drops of dichlorofluorescein solution (0.1 per cent Eastman indicator, catalog No. 373, in 70 per cent alcohol) were added, and the solution was titrated with the silver nitrate until the coagulated silver chloride precipitate acquired a distinct pink color. This pink color on the silver chloride was taken as the end point; the addition of a few more drops of the 0.05 *N* silver nitrate caused a pink color through the entire solution.

Table I. Typical Titrations

NaCl Grams	$AgNO_3$ Solution Cc.	Normality of $AgNO_3$ Solution
0.1171	40.40	0.04959
0.1195	41.22	0.04958
0.1187	40.95	0.04959
0.1184	40.93	0.04950

In Diothane analyses a sample of about 0.85 gram was dissolved in 80 cc. of 75 per cent alcohol and the titration was carried out with the 0.05 *N* silver nitrate solution in the manner described above. Some results are: 8.17 per cent chlorine, 4 batches (Nos. 67751, 67977, 68131, 68593); 8.18 per cent chlorine, 2 batches (Nos. 67369, 68362); 8.16 per cent chlorine, 1 batch (No. 67934); theoretical, 8.17 per cent chlorine.

Other organic hydrochlorides analyzed are:

α-Methylpiperidinopropanediol diphenylurethan hydrochloride, 8.01 per cent chlorine; theoretical, 7.92 per cent chlorine.
α-Piperidino-*n*-propylphenylcarbamate hydrochloride, 11.82 per cent chlorine; theoretical, 11.87 per cent chlorine.
Procaine hydrochloride, 13.07 per cent chlorine; theoretical, 13.05 per cent chlorine.

Titration of Bromides and Iodides

Samples of ammonium bromide, sodium bromide, and potassium iodide were analyzed for halogen with silver nitrate solution and dichlorofluorescein and the results compared with those obtained on the same samples with the standard Volhard method. The 0.05 *N* silver nitrate solution was gravimetrically standardized, and the 0.03 *N* potassium thiocyanate solution used in the Volhard titrations was standardized against the 0.05 *N* silver nitrate solution, with ferric alum as the indicator. The procedure used in the Volhard titrations was essentially that described in the United States Pharmacopoeia (*10*), except for the weights of sample and strengths of the standard solutions employed. The procedure used in the dichlorofluorescein titrations was the same as that described for the determination of chlorine in Diothane, except that the titrations were carried out in aqueous solution and that samples of about 0.2 gram of the bromides and 0.3 gram of the potassium iodide were used. These titrations were carried out in neutral or almost neutral solutions; strong light was avoided, as darkening of the silver halide precipitates made the end point more difficult to detect.

Table II. Titration of Bromide and Iodides

	Bromine		Iodine in
	Sodium bromide	Ammonium bromide	Potassium iodide
	%	%	%
Dichlorofluorescein method	77.96	82.13	76.74
Volhard method	77.93	82.11	76.73
Theoretical	77.66	81.59	76.45

These salts were all of U. S. P. quality; their deviations from theoretical halide content were due to the fact that they were not of reagent purity.

Discussion

Dichlorofluorescein is a satisfactory adsorption indicator for the argentometric titration of halides. Results of bromide and iodide titrations using this indicator compare favorably with those obtained with the standard Volhard method, but are usually slightly higher than those of the corresponding Volhard determinations; this can be expected from a consideration of the principles involved in the two methods. In one case, a slight excess of silver nitrate solution causes the dichlorofluorescein to be adsorbed on the silver halide particles and form its silver salt, which furnishes the end point; in the Volhard procedure, a slight excess of the thiocyanate solution produces the end point; since this excess of thiocyanate is subtracted from the quantity of silver nitrate solution added, the results should be slightly lower than in the titration in which dichlorofluorescein was used. Since only one standard solution need be used and no filtration is necessary, a determination employing dichlorofluorescein as the indicator can be carried out in less time than one in which the Volhard method is followed. Possible errors due to selective adsorption of the excess silver nitrate on the silver chloride precipitate and the filter paper in the Volhard procedure are eliminated, and chances of manipulative error are lessened.

The speed, accuracy, and broadness of application of this procedure indicate that it may prove of value in determinations of un-ionized halogen in which the treatment of the sample during the analysis forms the corresponding sodium halide. Such an application may be seen in the modification of the Stepanow method proposed by Cook and Cook (*2*), in which the sample is digested with absolute alcohol and metallic sodium, resulting in the formation of sodium halide in the reaction mixture. The titration liquid would then contain the sodium halide, among other things, in an alcohol-water solution; and, as has been shown in this paper, dichlorofluorescein is a suitable indicator for such titrations. Other applications may lie in the sodium peroxide fusion method for organic halogen (*6*) or in the liquid ammonia–sodium process (*11*), in which the sample is dissolved in liquid ammonia, treated with sodium, and the sodium halide determined. In the latter method Vaughn and Nieuwland used both the Fajans procedure, with eosin as an indicator, and the Volhard method for their titrations.

Since the completion of this manuscript a new paper (*5a*) by Kolthoff has discussed the theory of adsorption indicators in some detail.

Summary

Dichlorofluorescein has been used as an adsorption indicator in the argentometric titration of organic hydrochlorides dissolved in alcohol, and inorganic halides in alcohol or aqueous solutions. The analytical results have been within experimental error of the theoretical values on pure chemicals or of values obtained by the standard Volhard procedure on chemicals of ordinary commercial purity. Possible further applications of the method have been suggested.

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Gold-Cobalt Alloys Not Entirely Suitable for High-Grade Resistance Standards. Tests recently made at the National Bureau of Standards on alloys of gold and cobalt to determine their suitability for use in the construction of resistance standards show that, while some of these alloys are reasonably stable in resistance and have very small temperature coefficients of electrical resistance, their thermoelectric power against copper is very large. For this reason the bureau believes that they are inferior to gold-chromium alloys of about the same proportions. This conclusion is important since the unit of electrical resistance is maintained in the national standardizing laboratories by means of wire-wound standards. The national laboratories are interested in improving the quality of these standards, either by improved methods of construction or by the development of better resistance alloys.

Besides stability, resistance alloys should have a low-temperature coefficient of resistance and a low thermo-electric power against copper.

Digesting Biological Materials for Calcium and Phosphorus Analysis

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IT IS OFTEN necessary to make both calcium and phosphorus determinations on biological materials, particularly in vitamin D studies where the calcium and phosphorus ratio is of importance. In most cases it has been customary to prepare samples separately for the determination of the two elements, especially where the percentage of phosphorus in a material is high.

A rapid method of removing organic matter which will permit the determination of both calcium and phosphorus in the digest permits a saving of time on the part of the analyst and a saving of equipment and reagents to the laboratory. The following procedure is adapted to plant and animal material and has been found to give excellent results on such materials as feed concentrates, feces, and grasses. It should also be possible to determine mineral elements such as iron, magnesium, and others not forming insoluble perchlorate salts on this digest.

Procedure

Weighed samples of suitable size are placed in 500-ml. Kjeldahl flasks. Twenty to 30 ml. of concentrated nitric acid are added and the flasks are placed on asbestos gauzes over medium flames. The contents are boiled gently with frequent mixing until the samples pass into a semi-colloidal solution. The particles of material become swollen and gel-like, then disintegrate, producing a finer suspension or a solution. Experience will indicate at what time this occurs, and the speed of the digestion may be accelerated materially by determining the length of time required for the material being analyzed to reach this stage. For the materials reported in this paper the flames were so adjusted that the treatment took 30 to 45 minutes. Heating to dryness must be avoided.

Ten milliliters of 70 per cent perchloric acid are now added to each and the flasks are placed over free flames. Very low flames are necessary during the perchloric acid oxidation; best results are obtained when just sufficient heat is applied to keep the solution boiling. Only a fine point of the flame should impinge on the flask. Higher temperatures tend to drive off the perchloric acid without materially accelerating oxidation.

When fuming begins, the flame is so adjusted that only a trace of the perchloric acid fumes reaches the upper region of the Kjeldahl neck. The heating is continued until the solution is practically colorless or only a faint yellow color remains. The solution is allowed to cool slightly and 50 ml. of distilled water are added. Vigorous boiling occurs which drives out the remaining nitrogen dioxide fumes, leaving a clear solution.

The solution is filtered into a volumetric flask, and the Kjeldahl is thoroughly washed with distilled water. When the solution has cooled it is made to volume and aliquots are taken for analysis. Calcium and phosphorus determinations may be completed by the usual procedures.

Results

Data reported have been obtained by official methods (*1*). In the comparisons reported duplicate samples were digested by the proposed method and at the same time duplicate samples were prepared according to official methods. The comparisons are given in Tables I and II. A plus sign indicates that results by the proposed method are higher, while a minus sign indicates that they are lower than the results by official methods of preparing the sample. A and B indicate duplicate digestions. Results by the two methods agree closely and the differences are essentially the same as differences between duplicates by the same digestion method.

TABLE I. CALCIUM DETERMINATIONS

Digested with Nitric and Perchloric Acids				Ashed				Diff. between Acid Digestion and Ashing
A	B	Diff.	Av.	A	B	Diff.	Av.	
%	%	%	%	%	%	%	%	%
In Pasture Grass Volumetric Method								
0.94	0.93	0.01	0.94	0.93	0.93	0.00	0.93	+0.01
1.03	1.00	0.03	1.02	1.03	1.04	0.01	1.04	−0.02
0.98	0.98	0.00	0.98	0.97	0.99	0.02	0.98	0.00
1.07	1.08	0.01	1.08	1.06	1.08	0.02	1.07	+0.01
0.85	0.85	0.00	0.85	0.87	0.88	0.01	0.88	−0.03
0.87	0.89	0.02	0.88	0.88	0.84	0.04	0.86	+0.02
0.52	0.53	0.01	0.53	0.48	0.48	0.00	0.48	+0.05
0.57	0.59	0.02	0.58	0.57	0.56	0.01	0.57	+0.01
0.46	0.48	0.02	0.47	0.48	0.48	0.00	0.48	−0.01
0.34	0.33	0.01	0.34	0.34	0.34	0.00	0.34	0.00
In Poultry Feces, Volumetric Method								
0.67	0.72	0.05	0.70	0.73	0.69	0.04	0.71	−0.01
0.73	0.72	0.01	0.73	0.67	0.70	0.03	0.69	+0.04
3.87	3.89	0.02	3.88	3.89	3.82	0.07	3.86	+0.02
3.48	3.45	0.03	3.47	3.48	3.48	0.00	3.48	−0.01
3.56	3.56	0.00	3.56	3.51	3.53	0.02	3.52	+0.04
3.29	3.34	0.05	3.32	3.38	3.38	0.00	3.38	−0.06
3.56	3.57	0.01	3.57	3.61	3.57	0.04	3.59	−0.02
3 38	3.34	0.04	3.36	3.20	3.38	0.18	3.29	+0.07
3.24	3.23	0.01	3.24	3.20	3.25	0.05	3.23	+0.01
3.74	3.74	0.00	3.74	3.81	3.79	0.02	3.80	−0.06
3.29	3.27	0.02	3.28	3.25	3.25	0.00	3.25	+0.03
3.34	3.39	0.05	3.37	3.38	3.49	0.11	3.42	−0.05
In Poultry Feeds, Volumetric Method								
1.48	1.48	0.00	1.48	1.48	1.50	0.02	1.49	−0.01
2.27	2.30	0.03	2.29	2.28	2.24	0.04	2.26	+0.03
1.98	2.00	0.02	1.99	1.98	1.94	0.04	1.96	+0.08
1.90	1.94	0.04	1.92	2.00	1.99	0.01	2.00	0.00
1.70	1.73	0.03	1.72	1.86	1.88	0.02	1.87	−0.09
2.44	2.44	0.00	2.44	2.42	2.46	0.04	2.44	0.00
0.29	0.27	0.02	0.28	0.20	0.21	0.01	0.21	+0.06
0.21	0.26	0.05	0.24	0.22	0.26	0.04	0.24	0.00
0.20	0.25	0.05	0.23	0.24	0.28	0.04	0.26	−0.03
0.25	0.25	0.00	0.25	0.26	0.27	0.01	0.27	−0.02
3.23	3.24	0.01	3.24	3.17	3.19	0.02	3.18	+0.06

TABLE II. PHOSPHORUS DETERMINATIONS

Aliquots from Solutions Prepared for Calcium				Digested with Hydrochloric and Nitric Acids				Difference in Two Methods
A	B	Diff.	Av.	A	B	Diff.	Av.	
%	%	%	%	%	%	%	%	%
In Pasture Grass, Volumetric Method								
0.50	0.50	0.00	0.50	0.59	0.59	0.00	0.59	−0.09
0.35	0.35	0.00	0.35	0.35	0.39	0.04	0.37	−0.02
0.44	0.44	0.00	0.44	0.47	0.47	0.00	0.47	−0.03
0.48	0.48	0.00	0.48	0.45	0.44	0.01	0.45	−0.03
0.46	0.47	0.01	0.47	0.45	0.44	0.01	0.45	+0.02
0.44	0.43	0.01	0.44	0.44	0.44	0.00	0.44	0.00
0.63	0.63	0.00	0.63	0.55	0.54	0.01	0.55	+0.08
0.67	0.67	0.00	0.67	0.64	0.64	0.00	0.64	+0.03
0.58	0.59	0.01	0.59	0.56	0.55	0.01	0.56	+0.03
0.51	0.52	0.01	0.52	0.53	0.53	0.00	0.53	−0.01
In Poultry Feces, Gravimetric Method								
0.98	0.98	0.00	0.98	0.96	0.94	0.02	0.95	+0.03
1.08	1.10	0.02	1.09	1.06	1.11	0.05	1.09	0.00
1.53	1.54	0.01	1.54	1.51	1.51	0.00	1.51	+0.03
1.50	1.50	0.00	1.50	1.49	1.55	0.05	1.52	−0.02
1.48	1.51	0.03	1.50	1.49	1.46	0.03	1.48	+0.02
1.49	1.48	0.01	1.49	1.52	1.54	0.02	1.53	−0.04
1.59	1.59	0.00	1.59	1.49	1.63	0.14	1.56	+0.03
1.52	1.52	0.00	1.52	1.57	1.60	0.03	1.58	−0.06
1.51	1.49	0.02	1.50	1.60	1.54	0.06	1.57	−0.07
1.62	1.57	0.05	1.60	1.55	1.59	0.04	1.57	+0.03
1.68	1.66	0.02	1.67	1.60	1.66	0.06	1.63	+0.04
1.61	1.61	0.00	1.61	1.52	1.53	0.01	1.63	+0.08
In Poultry Feeds, Gravimetric Method								
				Digested with Nitric and Sulfuric Acids and Sodium Nitrate				
0.52	0.51	0.01	0.52	0.52	0.58	0.06	0.56	−0.04
0.99	1.01	0.02	1.00	0.96	0.84	0.12	0.90	+0.10
0.97	0.98	0.01	0.98	0.92	0.91	0.01	0.92	+0.06
1.00	1.00	0.00	1.00	0.97	0.95	0.02	0.96	+0.04
1.00	0.99	0.01	1.00	0.92	0.87	0.05	0.90	+0.10
1.11	1.08	0.03	1.10	1.06	1.11	0.05	1.09	+0.01
1.18	1.17	0.01	1.18	1.12	1.14	0.02	1.13	+0.05
0.57	0.56	0.01	0.56	0.61	0.61	0.00	0.61	−0.05
0.51	0.51	0.00	0.51	0.53	0.59	0.06	0.56	−0.05
0.55	0.51	0.04	0.53	0.61	0.51	0.10	0.56	−0.03
0.55	0.55	0.00	0.55	0.52	0.50	0.02	0.51	+0.04
2.30	2.29	0.01	2.30	2.25	2.16	0.09	2.21	+0.09

Discussion

Four-gram samples of pasture grass were digested in order to get sufficient calcium and phosphorus for the determinations. The time for digestion was about 1.5 hours. Two-gram samples of feed and feces were digested in 1.25 hours. When large amounts of potassium were present in the sample, more perchloric acid was required because of precipitation of potassium perchlorate.

The digestion is not difficult to conduct, but care must be taken that the sample is not boiled to dryness. Maximum speed of digestion will be obtained by noting carefully the time required for the nitric acid to emulsify the material. Insufficient heat tends to make the digestion lengthy, while excess heat boils off the nitric acid before its maximum effect is obtained. It is not advisable, therefore, to boil the nitric acid over a free flame. Best results, together with rapid digestion, were obtained by placing the flask on an asbestos gauze over a gas flame in a Kjeldahl digestion rack and turning on a full flame.

The digestion produces a clear solution in a short time, thus effecting a saving of time and apparatus when both calcium and phosphorus are to be determined on the same material. It is much more rapid than ashing and may therefore prove more efficient even when calcium or other elements alone are to be determined. Iron, magnesium, and other elements not forming insoluble perchlorate salts might also be determined on the digest.

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Impurities in White Sugars

VIII. Effects of Some Impurities on Decomposition of Sucrose during the Barley Candy Test

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Results obtained in the barley candy test for quality of sugar, a detailed description of which is given, are subject to variation due to slight differences in the routine of different operators, to differences in rate and duration of heating, and to different thermal properties of different pieces of apparatus. However, the results of a series of tests made by an experienced operator using the same utensils are comparable among themselves.

The effects of various salts and organic substances which may be present in white sugars were studied by making the candy test on a very pure standard sugar to which the nonsugar was added in known proportions. From the analyses of these candies it is seen that the nonsugars fall into three major groups: those of Group I increase the inversion of sucrose but inhibit caramelization or are without effect on either; those of Group II tend to inhibit inversion but increase the amount of caramelization; and those of Group III increase both the inversion and degree of caramelization. The auto-inversion of sucrose and the different effects of the nonsugars on the decomposition of sucrose during the candy test are explained by evidence showing that sucrose acquires an enhanced acidic nature at high temperatures and, together with its decomposition products, reacts with the nonsugars present in the sirup, causing greater inversion and less caramelization when the resultant hot sirups are acidic in reaction and less inversion and greater caramelization when they are alkaline in reaction. The increase in both inversion and caramelization in the presence of the nonsugars of Group III, which are acidic in reaction, is due to secondary reactions of the particular nonsugar with the invert sugar and other degradation products formed from the sucrose during the test. Salts of volatile or unstable acids react as alkaline salts.

It has long been a matter of general experience, especially among manufacturers of food products, that some commercial white sugars, when subjected to the elevated temperatures required in many processes, withstand the heating with less discoloration or with the formation of less invert sugar than others. Therefore there arose the practice of testing samples of new or prospective purchases of sugar (*25*) by quick, practical tests, the conditions of which approximate those to which the sugar would be subjected during the making of the finished food product. The cause of such variations in stability of different lots of sugar is ascribed to the effects of the impurities, or nonsugars, contained in small amounts in the white sugar, and hence it becomes of interest to know the effects of the commonly occurring nonsugars on the heat-resisting qualities of sucrose.

The practical tests developed for this purpose are of two types, the caramelization test, in which the dry sugar is heated, and the so-called "barley candy" test, in which a

small batch of hard candy is made from the sugar and water. The former is extensively used in Europe, where various modifications have been advanced from time to time. These were comprehensively studied by Pucherna (*33*), who proposed a standardized technic which he claims will yield reproducible results and which he used to study the effects of various nonsugars on a standard sugar. In this country, however, the barley candy test originally devised by Samuel C. Hooker of the American Sugar Refining Company (*28*) is generally used, because it more nearly approximates the actual conditions under which the sugar is to be used. To obtain reproducible results in either type of test, rigorously uniform conditions of rate and duration of heating and careful control of all factors in any way influencing these conditions must be maintained.

In the barley candy test, the personal variations of manipulation by different individuals in the timing and sequence of the motions necessary for carrying out the test have so great an influence on the candy produced that absolute reproduction of results by two different persons is very difficult of attainment, even though each follows the details of the test with the utmost precision. However, when one has become so familiar with the technic involved that his personal time reactions and rates have become automatic and standardized, he will be able to compare the candies made from different sugars, provided he not only has maintained uniform conditions of heating but also has used the same utensils throughout the entire series of tests, which is essential in order to eliminate variations of heating caused by the differing thermal properties and surface areas of different pieces of apparatus (*36*).

In order to arrive at a just evaluation of the quality of sugars by this test, no substance other than water should be used with the sugar. If some other substance is added in the test, as for example, glucose sirup, the interpretation of the results obtained is complicated by the fact that the material added and the impurities contained in it may have affected the heat-resisting qualities of the sugar. Even the mineral and organic compounds in the water used with the sugar may increase the discoloration or inversion of the sucrose (*23*), and therefore, if possible, the test should always be conducted with distilled water. Conversely, if a sugar is known to behave satisfactorily in the barley candy test, it may be adopted as a standard and other substances may be added to it or dissolved in the distilled water in order to ascertain the effect of the added material on the stability of the sugar toward heat.

All commercial white sugars, whether derived from sugar cane or sugar beets, contain nonsugar substances in amounts varying in the different grades from a few thousandths of 1 per cent in the purest sugars to about 0.5 per cent in the sugars of lower purity (*25*). Chemically these impurities are substances of many types, both organic and inorganic. Although at present it is impossible to detect most of them as individual substances, many of the inorganic elements and radicals and some of those classes of organic compounds, the individual members of which have common reactions due to like atomic groupings in their molecular structures, may be detected and even determined quantitatively. The total nonvolatile inorganic components are determined as the ash, which, of course, is susceptible of complete quantitative analysis. But, in interpreting such analyses, it must be borne in mind that they do not indicate the combinations originally present in the sugar because of pyrolytic changes which have taken place during the ashing process. Thus, sulfates and chlorides in the sugar may be partly lost (*15*), the former by reduction to sulfites or sulfides, the latter by reduction to chlorine or by displacement by less volatile acidic radicals. Carbonates, which are generally present in the ash, are formed, in part at least, by the interaction of basic oxides with the carbon dioxide produced by the burning of the sugar and its organic impurities. Nitrates and nitrites will be altered or entirely lost, and ammonium salts will be volatilized. Phosphorus, sulfur, and nitrogen in organic combinations may be lost or converted into inorganic compounds, depending on the amount and character of the basic oxides present and on the technic used in the incineration. The solution of the ash may be alkaline in reaction, whereas the solution of the sugar is nearly neutral or even slightly acid.

Methods have been described whereby it is possible to determine in white sugars small quantities of silica and organic and inorganic phosphates (*17*), of sulfates and organic and inorganic sulfites (*6*), of labile organic sulfur (*1*), of chlorides (*4*), and of total, protein, "amino acid," ammonium, nitrate, and nitrite nitrogen (*3*, *38*). Iron has been determined directly in the sugar (*21*), or may be determined in the ash. Aluminum, calcium, magnesium, sodium, and potassium must be determined in the ash. There are no methods of determining in white sugars such organic nonsugars as the saponins (*34*), individual proteins (*38*), gums (*25*, *29*), waxes (*12*), fats and oils (*29*), and polyphenolic compounds (*6*), all of which have been shown to be present and no doubt exert some influence on the decomposition and discoloration of sucrose during heating.

All barley candy tests made in the Carbohydrate Division are carried out in a copper casserole beaten from 0.16-cm. (0.0625-inch) stock, 11.6 cm. (4.56 inches) and 5.7 cm. (2.25 inches) in diameter at top and bottom, respectively, and 6.5 cm. (2.56 inches) deep, with a hollow handle 5 cm. (2 inches) long, made of the same stock, riveted to the side, into which is fitted a handle of oak about 17.5 cm. (7 inches) long.

Two hundred and twenty-seven grams (0.5 pound) of sugar and 90 cc. of distilled water are placed in the casserole, thoroughly mixed, and heated on a Chaddock burner in a place shielded from draughts with constant stirring, until all the sugar has dissolved, after which the sirup is left undisturbed until it commences to boil. The pressure and velocity of the gas admitted to the burner are so regulated that they are constant and bring the sirup to boiling in 5 to 5.5 minutes from the time heating was started. The casserole is then immediately covered with a 15-cm. (6-inch) watch glass, and the sirup is allowed to boil undisturbed. (If the sirup foams so badly on boiling that there is danger of its overflowing, the casserole is lifted momentarily from the burner to allow the foam to subside and the watch glass is placed in position as soon as the foam breaks and danger of overflowing has passed. When such foaming occurs it is noted as a characteristic of the sugar.)

Exactly 15 minutes after the heating was started the watch glass is removed and heating is continued, with constant stirring with a standard thermometer, until the temperature of the boiling sirup reaches 176° C. During the entire test the pressure and velocity of the gas are kept constant. The total time of heating is some interval between 21 and 25 minutes, and, if the gas is properly regulated, does not vary more than ±0.5 minute in the different tests of any series. As soon as the sirup has reached the temperature of 176° C. it is quickly poured out on a cold, clean, dry cooling plate of polished copper, 35 × 35 × 0.6 cm. (14 × 14 × 0.25 inches) in dimensions. When the candy plaque so formed has cooled and hardened, it is broken up, bottled, and used as soon as possible for analytical determinations.

Barley candies made from a high purity, low-ash sugar and distilled water were adopted as standard and compared with candies made from the same lot of sugar with distilled water in which there was dissolved or suspended the particular nonsugar whose effect on the sugar during heating was to be studied. In order to accentuate the effect of the nonsugar so that differences in the quantitative analyses of the candies might clearly be attributed to the effect of the added substance and not to the unavoidable experimental errors of technic and analysis, quantities of the nonsugars were used which in general greatly exceed those now to be found in white sugars. This also provided a means of over-

TABLE I. ANALYSES OF BARLEY CANDIES MADE WITH VARIOUS NONSUGARS

Nonsugar Added	Wt. Added	pH	Color	A Sucrose by Acid Inversion on Dry Solids	B Sucrose by Invertase on Dry Solids	C Reducing Substances as Invert Sugar on Dry Solids	A–B Hydrolyzable Anhydrides	100 − (A + C) Nonhydrolyzable Products
	Gram			%	%	%	%	%
None; average of 2 tests	0.0	4.7	29	96.67	96.36	1.95	0.31	1.38
Group I								
NaCl	0.1	4.7	26	95.64	94.33	2.86	1.31	1.50
NaCl	0.2	4.5	26	94.83	92.73	3.89	2.10	1.28
KCl	0.1	4.5	26	95.77	94.60	3.25	1.17	0.98
KCl	0.2	4.6	22	96.20	94.72	3.25	1.48	0.55
$BaCl_2.2H_2O$	0.2	4.8	15	88.16	80.25	11.99	7.91	−0.15
$CaCl_2$	0.2	3.9	56[a]	38.54	17.31	59.68	21.23	1.78
KNO_3	0.1	5.4	15	94.06	91.35	4.94	2.71	1.00
Na_2SO_4	0.2	4.3	25	96.10	95.71	2.55	0.39	1.35
K_2SO_4	0.2	4.5	23	96.91	95.45	2.38	1.46	0.71
$MgSO_4$	0.1	4.7	13	93.01	88.29	7.72	4.72	−0.73
KH_2PO_4	0.2	4.5	32	93.06	90.03	5.73	3.03	1.21
$CaCO_3$	0.2	6.5	29	96.52	95.99	1.99	0.53	1.49
$CaSO_4$	0.1	4.1	19	96.76	96.28	2.58	0.48	0.66
Potassium acid tartrate	0.1	3.9	21	88.37	83.28	12.36	5.09	−0.73
Group II								
$NaHCO_3$	0.1	4.7	140	96.76	97.13	0.85	−0.37	2.39
$NaHCO_3$	0.2	4.5	192	97.34	98.03	0.79	−0.69	1.87
Na_2CO_3; average of 2 tests	0.1	4.6	166	97.83	97.66	1.14	0.17	1.03
K_2CO_3	0.1	5.1	126	96.62	96.69	1.14	−0.07	2.24
$NaNO_2$	0.2	5.2	108	97.68	97.75	1.11	−0.07	1.21
Na_2SO_3	0.2	4.7	73	96.92	96.54	1.11	0.38	1.97
$NaC_2H_3O_2.3H_2O$	0.2	4.6	73	96.69	95.99	0.97	0.70	2.34
$Na_2HPO_4.2H_2O$	0.2	4.5	100	97.37	97.15	1.09	0.22	1.54
Sodium glycerophosphate	0.2	4.7	62	97.01	96.50	1.29	0.51	1.30
Calcium gluconate	0.2	4.2	38	97.20	96.66	0.84	0.54	1.96
Sodium citrate	0.2	4.7	71	98.07	98.00	1.01	0.07	0.92
Group III								
NH_4Cl	0.2	[b]	[b]	[b]	[b]	[b]		
$(NH_4)_2SO_4$	0.05	3.7	81	25.50	7.68	60.47	17.82	14.03
$NH_4.H_2PO_4$	0.1	3.1	90	27.66	9.37	69.33	18.29	3.01
Asparagin	0.1	4.7	45	95.93	94.00	3.73	1.93	0.34
Glutamic acid	0.05	4.1	57	59.59	43.59	41.23	16.00	−0.82
Glycine	0.05	4.7	59	97.11	96.26	2.39	0.85	0.50
$Fe_2(SO_4)_3.XH_2O$	0.02	4.1	[c]	52.07	34.21	45.57	17.86	2.36
$FeSO_4.7H_2O$	0.1	3.8	[d]	47.28	25.42	53.68	21.86	−0.96

[a] The color developed during the pouring and the early stages of cooling on the copper plate.
[b] Test could not be completed. Caramelization set in at 152° C., with very slow increase in temperature. After 22.5 minutes of heating, the temperature was only 155° and the sirup was black, smoking, and starting to froth over.
[c] Color was red-brown, not comparable with caramel.
[d] Color was greenish gray, not comparable with caramel.

coming any buffering effect of the small quantity of ash in the standard sugar. The data obtained from the analyses of these candies are tabulated in Table I.

The colors of the candies were determined by comparison with a standard caramel solution (*5*), and the values given in the table are percentages of the standard color as measured colorimetrically under illumination from a standard daylight lamp. Sucrose was determined by double polarimetric methods before and after hydrolysis with invertase (*7*) and with hydrochloric acid (*8*). Reducing substances were determined as invert sugar by the Munsen-Walker method (*9*). To eliminate errors due to the absorption of moisture from the air by the candies, the percentages of sucrose and reducing substances were calculated on the basis of total solids as determined by drying solutions of the candies on sand in a vacuum at 70° C. (*10*). The pH was determined colorimetrically in a solution of 15 grams of the candy in cold, neutral water.

The results indicate that the nonsugars fall into three major groups. Group I is composed of those which inhibit color formation while increasing the amount of reducing substances, or are without material effect on either. The nonsugars of this group are salts whose aqueous solutions are neutral or acidic in reaction. Group II includes those nonsugars which increase the color formation but decrease the amount of reducing substances. These nonsugars are salts which have an alkaline reaction in water solution and also salts of strong bases with easily volatile acids or with unstable acids derived from very volatile anhydrides. Group III is made up of those nonsugars which increase both the formation of color and of reducing substances. These are ammonium salts, amino acids and amides, and iron salts.

Discussion

NONSUGARS AND THE INVERSION OF SUCROSE. An explanation of the action of the various nonsugars may be found by considering the properties of sucrose, invert sugar, and their decomposition products in conjunction with those of water and of the nonsugars themselves. Prinsen-Geerligs (*32*), Dedek and Terechov (*19*), Stearn (*37*), Urban et al. (*40*), Pucherna (*33*), and others have demonstrated that sucrose itself has weakly acidic properties (cf. Percival, *30*). The quantity of hydrogen ions liberated from sucrose is apparently enhanced by elevation of temperature, and this causes the so-called "auto-inversion" of pure sucrose by heat (*36*). The ionization of water is also increased at higher temperatures (*13*, *39*) and is, therefore, a contributing factor in the inversion of sucrose, but, from the evidence presented in the following paragraphs, it seems to be of minor significance in comparison with the increased ionization of sucrose.

The auto-inversion of sucrose is strikingly shown by the following experiments, which were made with dry sugars according to Pucherna's technic (*33*) for the caramelization test. Because of the fact that he used as standard a sugar having an ash content of 0.013 per cent, which, as will be shown, is just above a critical value, Pucherna missed some interesting observations in regard to the instability of pure sucrose toward heat. After having been dried for 2 hours at 100° C., 6.5-gram samples of the sugars were heated for 15 minutes in test tubes in an oil bath preheated to and maintained constant at 170° C. The samples were removed, allowed to cool in the air, and analyzed. A few typical results are given in Table II.

From this table it is evident that sugars having an ash content of about 0.010 per cent or less may undergo much greater inversion by heat than sugars of higher ash content, and that as little as 0.010 per cent of ash may reduce very efficiently the degree of auto-inversion of the sucrose. The different degrees of inversion shown by the sugars having an ash content of approximately 0.010 per cent or less must be caused by the differing composition and proportion of the nonsugars present in the different lots of sugar from which the samples were taken. When this test is carried out with dry sugars at 170° C., the ash content of 0.010 per cent is thus seen to be an average critical value, in that, with sugars whose nonsugars are of usual composition, this quantity of ash is just sufficient to act as a buffer against the increased liberation of hydrogen ions from the sucrose under the conditions of the test. If a different temperature is used in the test, a different value for this critical ash content is to be expected. If the sugars contain unusual or abnormal impurities, the critical value will again be altered, due to the different buffering effects of the ash constituents and of the other nonsugars present. The organic and volatile impurities also play a part in the inversion of sucrose and, if present in abnormal quantities, may require greater quantities of ash for effective buffering.

In the experiments in which he added sodium acetate, Pucherna noted a distinct odor of acetic acid rising from the mixtures during the heating. He ascribed this to the expulsion of acetic acid from the sodium acetate by the sucrose, which was reacting with the sodium acetate in the manner of a nonvolatile acid at elevated temperature, expelling the more volatile acetic acid. Although there may be some doubt of the validity of this explanation, because his standard sugar, containing 0.013 per cent of ash, might have contained constituents capable of liberating small quantities of acetic acid by acid exchange at the high temperature, his idea is probably correct.

The following experiments show the acidic nature of sucrose in aqueous solution at the boiling point:

Two distilling flasks were connected to condensers whose ends dipped into duplicate solutions made by mixing 25 cc. of 1 per cent sulfanilic acid solution, 25 cc. of 0.5 per cent α-naphthylamine hydrochloride solution (*11*), and 50 cc. of distilled water. In each flask were placed 500 cc. of a 0.1 per cent solution of recrystallized sodium nitrite of neutral reaction, and, after 25 grams of sugar containing 0.002 per cent ash had been dissolved in one of them, both solutions were slowly and simultaneously distilled. Before the solutions began to boil, the reagent in the receiver connected with the solution containing the sugar began to turn pink, indicating the presence of nitrous acid, while the other reagent remained colorless until the nitrite solution began to boil. After 5 minutes of boiling, the reagent into which the sugar solution was being distilled was very much deeper in color than the other. Before 15 minutes had elapsed, so much nitrous acid had been displaced from the sugar solution that the red dye formed in the reagent began to flocculate. At the end of 25 minutes the reagent receiving the distillate from the simple nitrite solution was still a clear red with no trace of a precipitate. The greater production of dye in the receiver from the sugar solution shows that this solution contained more hydrogen ions than the other, resulting in the liberation of larger quantities of nitrous acid, which in turn decomposed into its gaseous anhydride, N_2O_3. The source of this larger quantity of hydrogen ions can only be the sucrose, which must have ionized sufficiently to act as a nonvolatile acid and displace the unstable nitrous acid from its salt. Similar results were also obtained with more concentrated sugar solutions, which contained up to 255 grams of sugar in 100 cc. of nitrite solution.

Since sucrose in solution shows this tendency to furnish hydrogen ions at high temperatures, the inverting action of the salts in Table I becomes apparent from the following considerations. The ash in very pure sugar, such as was used for the standard, is not sufficient in quantity to buffer the solution against the ionization of sucrose, and the hydrogen ions liberated from the sugar cause the hydrolysis of un-ionized sugar molecules to an extent dependent on the hydrogen-ion concentration. This accounts for the auto-inversion of sucrose by heat, which is more pronounced in Pucherna's method (Table II) than in the barley candy test.

In the presence of the neutral salts of Group I (with the exception of calcium carbonate and sulfate) there are formed in the hot solution the ions of strong acids which do not easily volatilize from very dilute solutions until high temperatures and high concentrations of the acids and of hydrogen ions (*39*) have been reached. Therefore, here these acids are not removed until late in the cooking of the candy (if at all), and their strong inverting power results in the hydrolysis of larger quantities of sucrose. The results agree with this reasoning. The concentration of the constant boiling mixture of hydrochloric acid is lower than that of the constant boiling mixture of nitric acid and, as Table I shows, less invert sugar is formed in the presence of potassium chloride than in that of potassium nitrate. When the sulfates of the alkalies and of calcium are present, the fact that less invert sugar is formed, although sulfuric acid is not volatile at the temperatures of the candy test, is in agreement with the fact that sulfuric acid is a weaker, less powerfully inverting acid than hydrochloric or nitric acids and the hydrogen ions first liberated from the sucrose would react with the sulfate ion to form the HSO_4^- ion, which has relatively little inverting power. In all cases, acidic decomposition products of either sucrose or invert sugar contribute to the formation of invert sugar in virtue both of their own acidity (*14*) and of the argument just presented.

Table II. Analyses of Sugars of Various Ash Contents after Having Been Heated 15 Minutes at 170° C.

Sugar	Ash	Reducing Substances as Invert Sugar	Color Original	Color Alkalinized
	%	%		
1	0.001	8.75	19	600
		9.34	18	584
2	0.004	8.70	12	628
		9.20	12	576
3	0.007	34.68	9	552
		30.64	10	520
4	0.008	0.30	16	18
5	0.009	0.47	26	30
6	0.010	1.61	32	152
7	0.010	0.46	22	28
8	0.012	2.44	19	360
9	0.015	0.61	34	50
10	0.017	0.61	22	32
11	0.022	0.63	32	35
12	0.040	0.54	29	56
13	0.095	0.68	41	71
14	0.124	0.44	28	38
15	0.254	0.54	49	64

The greater inversion in the presence of the chlorides of the alkaline earths is in line with the fact that these salts are more inclined to hydrolyze into free acid and basic salts than are the corresponding salts of the alkali metals. In this respect, calcium chloride is more unstable than barium chloride, and it is found that the former is more powerfully active as an inverting agent in the candy test than the latter. The fact that calcium carbonate is an excellent buffer is well known, and is shown in Table I by the facts that it causes no change in the quantity of invert sugar formed as compared with the standard candy, and that the pH of the candy has the exceptionally high value of 6.5.

Those nonsugars of Group II which have an alkaline reaction in aqueous solution act as buffering agents against the acidic properties of sucrose and, by suppressing the concentration of hydrogen ions, tend to inhibit the inversion of sucrose. Sodium nitrite acts in the same way because of the instability of nitrous acid and the volatility of its anhydride, as already discussed. The removal of the nitrite

ion leaves an alkaline solution, resulting in the suppression of the ionization of the sucrose and therefore in a decreased degree of inversion.

The nonsugars of Group III are acidic in water solution and therefore cause inversion of sucrose. The small quantity of glycine used and its weak acidic nature (*18*) are probably responsible for the very slight increase in reducing substances formed and for no appreciable loss of sucrose in comparison with the standard. It is placed in Group III rather than in Group II because the quantity of reducing substances formed indicates that it is lacking in the buffering effect characteristic of Group II.

Nonsugars and Production of Color during the Candy Test. The decomposition of sucrose in acid solution results in the formation of invert sugar as the first product. In alkaline solutions, the decomposition seems to follow a different course which is still but little understood (*22, 35*). For the purposes of this discussion, however, it will suffice to assume that the reaction is a decomposition of sucrose with the formation, among other products, of reducing substances of true aldehydic or ketonic types and also that a slight degree of inversion takes place in consequence of localized momentary liberation of hydrogen ions. With this assumption, the discoloration or caramelization of sugars during the test results from the further decomposition by heat of invert sugar and the reducing substances containing the carbonyl group in solutions of differing concentrations of hydrogen ions.

When heated alone or with very dilute or weak acids, both the sugars comprising invert sugar pass, with little discoloration, into a series of anhydrides, ranging from simple anhydrides such as glucosan, levulosan, and ω-oxymethylfurfural, through reversion products of the oligosaccharide type to highly polymerized, more completely dehydrated products of colloidal nature. Evidence that such a series of dehydration products is formed in the candy test may be deduced from Table I. Many of the simpler anhydrides of dextrose and of levulose are not only dextro-rotatory—for example, α-*d*-glucosan, $[\alpha] = +69.4°$; levulosan, $[\alpha] = +18.6°$—but are also hydrolyzed back to the original sugars by strong acid (*41*), such as is used in determining sucrose by acid inversion. Hence the value for sucrose as determined in the double polarimetric method using acid (column A, Table I) is generally in excess of that as determined in the method using invertase (column B, Table I) which acts only on the sucrose. The difference in the values obtained by the two methods (A − B) may, therefore, be taken as a rough approximation of the quantity of those anhydrides and reversion products formed during the test which are hydrolyzed by acids to invert sugar. It is to be noted that, in Group I, this difference is generally greater the larger the percentage of reducing substances. Likewise, 100 per cent minus the sum of the values for sucrose by acid inversion (column A) and of the reducing substances (column C), [100 − (A + C)], furnishes a rough approximation of the quantity of nonreducing and nonhydrolyzable anhydrides and degradation products, including those which, by progressive and extensive dehydration and polymerization as the boiling sirup loses more and more water by evaporation during the later part of the test, have become colloidal. [The negative values in both columns, A − B and 100 − (A + C), arise from the accumulation of experimental errors and indicate that the values are only rough approximations.]

In alkaline solution, however, both dextrose and levulose undergo deep-seated and complex isomerizations and degradations accompanied by caramelization and oxidation (*2, 16, 21, 42*). Furthermore, the reducing substances formed by the degradation of the sugars in alkaline solutions, especially those containing an aldehydic carbonyl group, of which methyl glyoxal is one (*21*), show the property, characteristic of aldehydes, of undergoing condensations and polymerizations in alkaline media, with formation of highly colored colloidal matter. Thus the invert sugar formed by localized hydrolysis of sucrose and the aldehydes formed by degradation of sucrose and invert sugar are quickly converted into organic nonsugars which do not hydrolyze in acid solution to regenerate the original reducing substances. The differences between the sucrose values (A − B) are, therefore, smaller in the presence of the alkaline or potentially alkaline nonsugars of Group II than in that of the acidic or potentially acidic substances of Group I. Also a greater formation of nonhydrolyzable condensation products is indicated by the fact that 100 per cent minus the sum of the sucrose by acid inversion and the reducing substances [100 − (A + C)] is generally greater in Group II than in Group I.

Similar considerations applied to the substances in Group III indicate in general the formation of large amounts of anhydrides capable of being hydrolyzed back to invert sugar by acid (A − B) and also, in some instances, the production of large amounts of products of the nonhydrolyzable type [100 − (A + C)], some of which arise from reaction of invert sugar and its degradation products with the particular nonsugar added in the test (*27*).

Lundén (*26*) emphasizes the fact that some of the colored substances in sugar have properties resembling those of acid-alkali indicators, since they are colorless or pale yellow in acid solution and brown in alkaline solution. The transition point is not sharp because the coloring matter is not homogeneous. He therefore recommends that all sugar solutions be adjusted to a definite pH before measuring the color as a means of determining the quality of a sugar. However, since the candy test is for the purpose of testing the color produced under conditions approaching those of actual use, this adjustment of pH does not seem necessary for practical testing.

Pucherna (*33*) makes two color determinations, one on the 0.5 *N* solution of the heated sugar and a second after heating the 0.5 *N* solution for 10 minutes on the steam bath with 0.5 cc. of 2 *N* sodium hydroxide (the "original" and "alkalinized" colors, respectively, of Table II). He interprets the increase in color as a measure of the quantity of the invert sugar formed during the test, since invert sugar in alkaline solution decomposes with the formation of intensely colored products. Table II shows that this procedure gives a rough approximation of the invert sugar formed only in the cases of those sugars which have an ash content greater than 0.01 per cent. Since these sugars also show greater color formation without the treatment with alkali, the second determination, that of the alkalinized color, seems unnecessary for practical purposes.

Although the coloring matters produced have the properties of indicators, there is apparently no relationship between the colors and the pH of the solutions of the candies in cold neutral water as recorded in Table I. A brief consideration of the effects of temperature on the ionization of water and of the nature of the candy will show that such a relationship is not necessarily to be expected. While the ionization constants and the pH of the neutral point in highly concentrated sugar solutions at high temperatures are unknown, it has been demonstrated that the ionization of pure water is progressively increased by elevation of the temperature and therefore that the pH of the neutral point of water decreases as the temperature increases (*13*). It is reasonable to suppose that the same phenomenon takes place in sugar solutions but to a different degree.

The boiling sirup in the candy test is a supersaturated sugar solution which, when suddenly cooled by pouring on the cold copper plate, becomes an amorphous glass of super-

cooled molten sugar of great viscosity and low water content. This sudden change in temperature presumably fixes the colored substances as they existed in the hot sirup, and changes them into strongly dehydrated colloids with loss of their sensitivity as indicators until they are redispersed by the action of relatively high concentrations of hydrogen or hydroxyl ions. Thus the colors of the candies seem to indicate conditions of ionization, pH and buffering during the candy test differing from those obtaining at ordinary temperatures, and may be considered as indicators showing roughly the conditions of acidity or alkalinity in the sirup at 176° C. On long standing, after the candy has come to more stable conditions by the crystallization of the sucrose, whereby the colored material and other nonsugars accumulate in the film of less viscous sirup in the interstices between the crystals (*24*), the color, as determined by comparison of a fresh solution of the candy with standard caramel solution (*5*), gradually increases. This would indicate either a slow oxidation of the coloring matter to more intensely colored products, or, in Group I, an adjustment of the color to the pH of the candy at ordinary temperatures made possible by the increased mobility of ions in the less viscous film of sirup.

The dark color of the candy containing calcium chloride is definitely due to decomposition reactions subsequent to the heating. The boiling sirup at 176° C. is practically colorless, but darkens as it is poured out and the darkening continues while the plaque is cooling. There is also an evolution of a small amount of smoke. This discoloration may be due either to oxidation or to further dehydration of some of the practically colorless decomposition products of invert sugar.

The slight increase in color in the presence of potassium dihydrogen phosphate is probably due to cumulative experimental errors and, in any case, is so slight as to be negligible.

The nitrogenous nonsugars of Group III (Table I) cause the production of highly colored candies in spite of the acidity indicated by the high percentage of reducing substances, because they react so readily with invert sugar to form the intensely colored melanoidins of Maillard (*27*). The complete caramelization of the sugar in the presence of ammonium chloride is in harmony with the frequent use of small quantities of ammonium salts in the commercial production of caramel.

The colors of the candies containing iron salts are not comparable with those of caramel solutions because of the well-known fact that iron enters into reaction with polyhydric alcohols to form intensely colored complex compounds and because of charring of the sugars by the free acid liberated by hydrolysis of the iron salts. An experiment with 0.2 gram of ferric chloride resulted in complete caramelization and frothing at about 150° C., as in the case of ammonium chloride. This is in agreement with the generally recognized fact that iron is an extremely objectionable impurity (*31*) and is to be eliminated from sugars and sugar products as far as possible.

Acknowledgment

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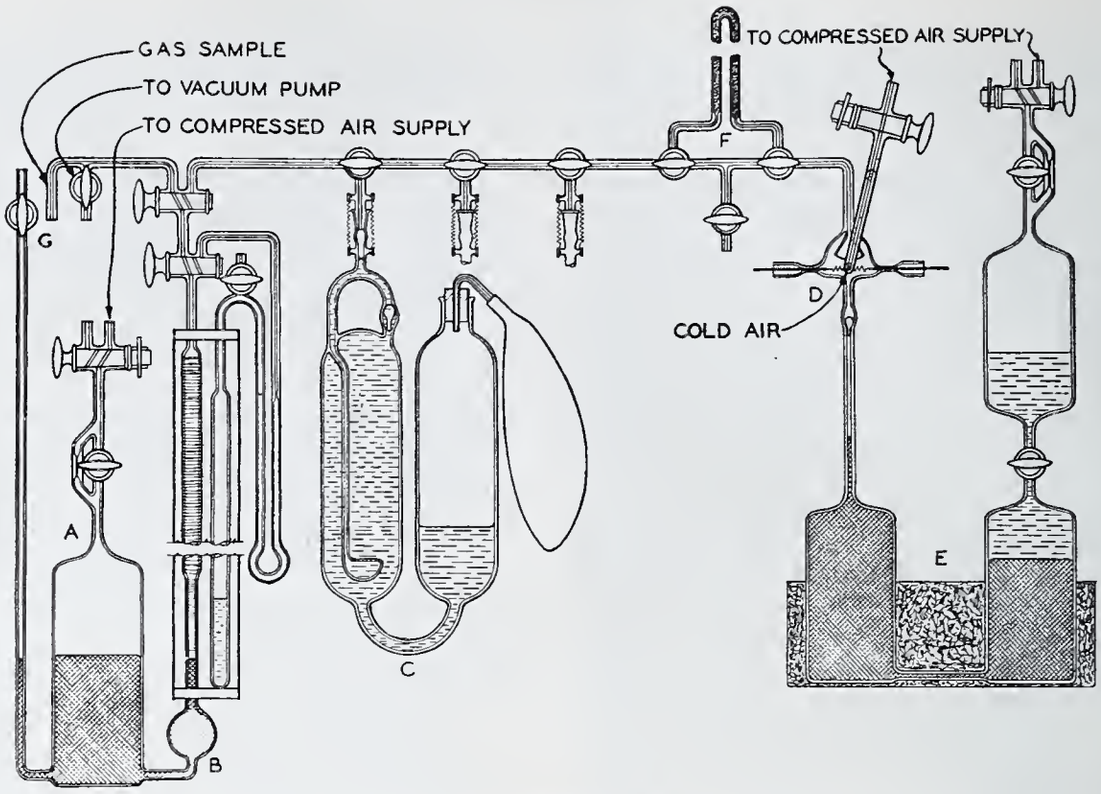

FIGURE 1. APPARATUS FOR MODIFIED FLUE-GAS ANALYSIS

A. Assembly, including capillary by-pass for raising and lowering mercury in buret by compressed air
B. Buret. Volume, 80 ml. Graduations, 0.1 ml. and 0.02 ml.
C. Gas-absorption chamber, including check valve and glass device for breaking up gas into fine bubbles
D. Total combustion chamber. Spiral platinum wire, No. 30, 11 cm. long. Tungsten lead-in wires
E. Assembly, including check valve and mercury reservoir for combustion chamber
F. Slow-combustion copper oxide tube
G. Excess-pressure safety valve

Analysis of Combustibles in Flue Gas

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A laboratory procedure for flue-gas analysis, designed to estimate the loss due to incomplete combustion, is described, including a comparison of the results of field and laboratory procedures of flue-gas analysis from a recent efficiency test on a modern steam-generating unit. A laboratory apparatus which, employing a synthetic flue gas, is capable of measuring this loss directly is also described.

IN AN ATTEMPT to reduce the unaccounted-for loss in steam-generator efficiency tests, a study has been made of methods for estimating the combustible gas stack loss. The standard method of gas analysis (*2*, *3*) calls for separate determinations of carbon dioxide (acidic oxides), oxygen, unsaturates, carbon monoxide, hydrogen, and hydrocarbon (assumed to be methane and ethane), each of which may be reasonably expected to be present in flue gas in varying amounts. Although a high degree of precision may be obtained with care when using the apparatus described by the Bureau of Mines (*2*), it was considered advisable to modify the standard procedure somewhat for flue-gas analysis in appreciation of the various factors connected with steam-generator efficiency tests—uninterruption of sampling during the test, the presence of small amounts of combustibles, the ultimate use of the data in heat calculations, and the accuracy of the determination of the other test data.

An apparatus for the direct determination (catalytic combustion) of the combustibles in flue gas has also been developed. Through the use of a synthetic flue gas, the laboratory stage of development has been completed, and valuable information can be obtained at a power station by means of this apparatus.

Modified Flue-Gas Analysis

Watson and Ceaglske (*12*) describe a modified procedure of gaseous fuel analysis in which a triple combustion method is employed for gas samples of a high calorific content. In the authors' work, carbon monoxide was determined independently and the standard procedure shortened, thus reducing the opportunity for error because fewer manipulations are necessary and at the same time yielding results of value for steam-generator efficiency tests. The determination of acidic oxides followed by total combustion over a heated platinum spiral completes the analysis.

The constructional details of the method of obtaining representative laboratory samples are described elsewhere (*5*). A 2-liter gas sample was taken continuously over a period of 4 hours, during which time the gas from the stack slowly displaced mercury in a Pyrex sampling bottle. The use of mercury both in obtaining the laboratory sample and as the confining liquid in the buret avoided the uncertainty of the solvent action of other liquids. Samples were taken at 15-minute intervals for analysis in the standard Orsat apparatus in the field.

The procedure employed in the laboratory consisted of (*a*) measurement of sample of such volume that the reading oc-

curred on the constricted portion of the buret; (*b*) absorption of acidic oxides and (*c*) of oxygen in the usual manner; (*d*) addition of oxygen previously purified and stored in a third absorption pipet, in an amount such that the volume could be read in the constricted section of the buret; and (*e*) total combustion of all combustibles over a heated platinum spiral followed by the observation of the total shrinkage and of the total carbon dioxide formed. It followed that variations of 0.01 cc. in the original volume of the sample, the shrinkage, and the carbon dioxide formed on total combustion could be detected, since the constricted section of the buret was graduated to 0.02 cc. Furthermore, it is obvious that step *c* may be omitted unless a check on the field determination of oxygen is desired.

The novel features of the apparatus (Figure 1) include the transfer of gas by means of a mercury piston and compressed air, a constriction in the buret to obtain small volume changes, pressure stopcocks (*4*), glass-seated valves in the absorption pipets (*1*), and a combustion pipet of small volume protected by a glass-seated check valve. The volume (5 cc.) of the combustion chamber must be included in the manifold error but may be made small if filled with nitrogen. Ordinarily, if the hydrocarbon content in the flue gas was low (0.1 per cent) the carbon dioxide remaining in the manifold was neglected, but when greater amounts were present the gas, after removal of the carbon dioxide, was passed into the combustion assembly, followed by a repetition of the procedure for removing carbon dioxide. The combustion of the residual gas remaining after analyses did not show a change in volume greater than 0.01 cc.

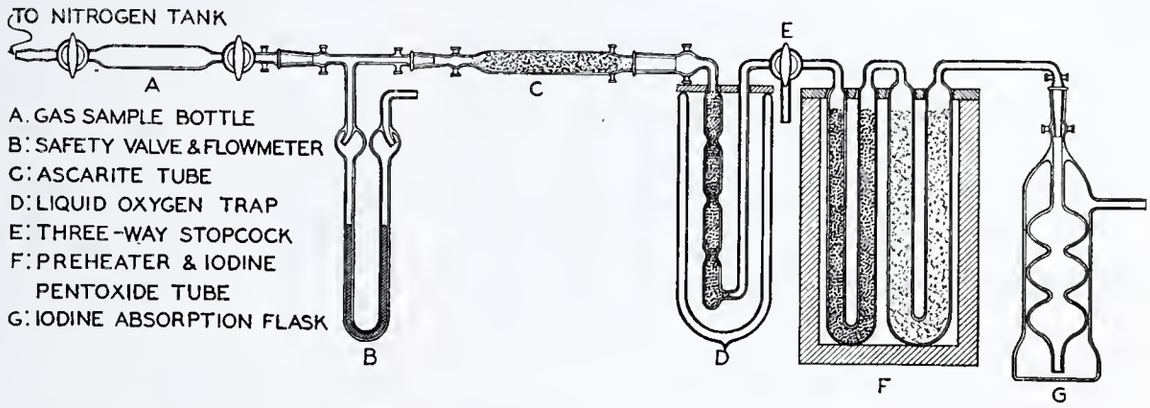

FIGURE 2. APPARATUS FOR DETERMINATION OF CARBON MONOXIDE

TABLE I. ANALYTICAL DATA ON POSSIBLE HYDROCARBONS IN FLUE GAS

Hydrocarbon	Volumetric Ratio upon Combustion[a]	Heat of Combustion, Kg.-cal./g.	Carbon Dioxide Formed per Gram of Hydrocarbon
			Grams
Methane	2	13.1	2.7
Ethane	1.25	12.2	2.9
Propane	1	12.0	3.0
Butane	0.875	11.7	3.0
Ethylene	1	11.9	3.1
Propylene	0.835	11.7	3.1
Butylene	0.75	11.5	3.1
Amylene	0.7	11.5	3.1
Acetylene	0.75	12.0	3.4
Propine	0.67	11.8	3.3
Butine	0.625	..	3.3
Pentine	0.6	..	3.2
Benzene	0.42	10.1	3.4
Weighted average	1	12	3.0

[a] Ratio between shrinkage and carbon dioxide formed.

The heat equivalent of the carbon dioxide formed on combustion was calculated from the approximate heat data in Table I. Thus a gram of the mixture of the listed hydrocarbons would yield 3 grams of carbon dioxide and liberate 12 kg.-calories upon combustion. This statement is true to roughly 10 per cent, but a result of this accuracy is satisfactory in reducing the unaccounted-for loss in steam-generator efficiency tests. The following equations illustrate the method in which the gas analysis data were used:

Let A = per cent of carbon monoxide (determined independently)
B = per cent of carbon dioxide found on total combustion
C = per cent of shrinkage observed

$B - A$ = per cent of hydrocarbon (1)

$C - {}^1/_2 A$ = per cent of shrinkage due to hydrocarbon and hydrogen (2)

$C - {}^1/_2 A - (B - A)$ = per cent of shrinkage due to hydrogen (3)

${}^2/_3 [C - {}^1/_2 A - (B - A)]$ = per cent of hydrogen (4)

The assumption made in Equation 3 follows from an analysis of the relation between the shrinkage data and the carbon dioxide formed on combustion found also in Table I. The formation of the hydrocarbons by thermal decomposition and other secondary reactions in the flue gas renders it practically impossible to predict their chemical nature but, in order to utilize the experimental data, the choice of a ratio of 2 enables one to say that there is definitely present the percentage of hydrogen thus calculated, and a ratio of 1 appears more likely in view of a large amount of test data on flue-gas analysis. Thus, in a group of fifty analyses, only ten showed the presence of hydrogen using a ratio of 1 and but five samples contained hydrogen assuming a ratio of 2. The authors are aware of certain absurdities under special cases in which particular mixtures of hydrocarbons and hydrogen may be assumed (*3*, p. 128) but these inconsistencies are not so glaring on a heat of combustion basis. The application of the analytical results in equation form to steam-generator efficiency tests is given in formulas for estimating combustible stack loss in steam-generator efficiency tests, where quantities refer to wet flue gas.

$\frac{V_{HC} \times w_{CO_2} \times W \times 4000}{D}$ = loss in calories per gram of coal due to presence of hydrocarbons in flue gas

$\frac{V_{H_2} \times W \times 2.784}{D}$ = loss in calories per gram of coal due to presence of hydrogen in flue gas

$\frac{V_{CO} \times W \times 2.765}{D}$ = loss in calories per gram of coal due to presence of carbon monoxide in flue gas

V_{HC} = volume in cc. of carbon dioxide resulting from combustion of hydrocarbon in 1 cc. of flue gas
V_{H_2}, V_{CO} = volumes in cc. of hydrogen and carbon monoxide, respectively, in 1 cc. of flue gas
w_{CO_2} = weight in grams of 1 cc. of carbon dioxide at 25° C. and 1 atmosphere pressure
W = weight in grams of flue gas per gram of coal
D = density of flue gas at 25° C. and 1 atmosphere pressure
4000 = calories per gram of carbon dioxide resulting from combustion of hydrocarbons (Table I)

The apparatus for the independent determination of carbon monoxide is shown in Figure 2 in which interchangeable ground joints were used throughout. The type of apparatus was originally described by Teague (*9*). More recently, Vandaveer and Gregg (*11*) have pointed out the chemical nature of certain interfering substances when iodine pentoxide was used in the determination of carbon monoxide. The

vapor pressure of these substances (aldehydes and ethylenic unsaturates) has not been determined for the individual members of the two classes of compounds, but in a paper by Leighton and Blacet (*6*) attention is called to the fact that propionaldehyde was not entirely removed by a liquid air trap. A special composition of illuminating gas (approximately 1 per cent combustible) also gave evidence in this laboratory of a substance which was slowly carried through the liquid oxygen trap by the carrier gas, nitrogen, and which was oxidized by the iodine pentoxide. Qualitative tests indicated that aldehydes were absent and that the interfering substance was of the unsaturated class. The data in Table II indicate the action of chromic–concentrated sulfuric acid mixture (*11*) in removing the undesirable constituents from identical samples of gas of special composition from a cylinder. The chromic acid absorption flask (not shown in Figure 2) was inserted in the train before the ascarite tube.

The data indicate that chromic acid, heated by a bath of boiling water, was effective in removing the harmful constituents, and that the method of Teague is open to serious criticism with certain gas mixtures. Several samples of flue gas gave the same result with or without the chromic acid absorption flask but this was suspected, since a zero blank was obtained at the completion of each analysis.

Table II. Removal of Interfering Substances in the Determination of Carbon Monoxide

(Rate of flow of carrier gas, 45 cc. per minute)

Sample Volume	Time Increments	Liberated Iodine as Carbon Monoxide Increments	Remarks
Cc.	Min.	%	
40	60	0.11	No chromic acid
	45	0.12	
	45	0.00	
40	60	0.10	Chromic acid at room temperature
	45	0.08	
	45	0.00	
40	60	0.09	Chromic acid heated by a bath of boiling water
	45	0.00	

Table III. Comparison of Field and Laboratory Flue-Gas Analyses

Run	1	2	3	4	5	6	7	8	9	10
	Per Cent by Volume, Wet									
Laboratory:										
Hydrogen	0.03	0.03	0.04	0.03	0	0	0.05	0.04	0.04	0.06
Hydrocarbon	0.09	0.21	0.04	0.03	0.07	0.06	0.07	0.07	0.07	0.02
Carbon monoxide	0.05	0.20	0.13	0.09	0.05	0.03	0.05	0.08	0.12	0.26
Oxygen	4.7	4.1	4.4	4.9	4.6	4.5	4.6	4.5	4.9	4.1
Carbon dioxide	14.6	14.8	14.6	14.3	14.4	14.5	14.1	14.4	14.3	14.6
Field:										
Carbon monoxide	0.05	0.08	0.04	0.03	0.03	0.02	0.04	0.07	0.04	0.06
Oxygen	3.7	3.4	3.6	4.0	3.7	4.0	4.1	4.0	3.8	3.4
Carbon dioxide	14.8	15.0	14.9	14.5	14.8	14.5	14.4	14.5	14.6	15.1
	Combustible Energy Loss, Per Cent									
Hydrogen	0.1	0.1	0.2	0.1	0	0	0.2	0.2	0.1	0.2
Hydrocarbon	1.1	2.4	0.5	0.4	0.8	0.7	0.9	0.9	0.8	0.2
Carbon monoxide (lab.)	0.2	0.7	0.5	0.3	0.2	0.1	0.2	0.3	0.4	0.9

In Table III, the analytical results (*5*) from the laboratory and field procedures (Orsat) are compared. Each laboratory percentage represents an average of 6 analyses while, over the same period of time (24 hours), each field percentage represents an average of 96 analyses. The field carbon monoxide determinations (ammoniacal cuprous chloride) gave lower results than the laboratory method and the divergence apparently increased with larger percentages of carbon monoxide. Oxygen in the field (alkaline pyrogallate) was unexpectedly much lower than in the laboratory (sodium hyposulfite). The absorption of thermal radiation from the steam generator by the dark-colored alkaline pyrogallate, thus raising the temperature of the solution, was possibly responsible for this difference. The carbon dioxide determinations in the field and laboratory are in quite good agreement. The equivalent percentage of the combustibles (*5*) on the thermal efficiency basis is also included in Table III.

Catalytic Combustion Method

The value of the direct determination of the calorific content of flue gas lies in the fact that in one measurement the most significant property of the gas sample is obtained relative to the efficiency of the combustion of fuel. The results of experiments with an apparatus designed for the above purpose are given.

In Figure 3, the apparatus is shown which was finally adopted after considerable previous experimentation with several devices of a filament type. The external heater and insulation were the commercial type of combustion furnace. Nitrogen, oxygen, and the combustible gas from cylinders were metered separately by means of flowmeters (*14*) and then led into a mixing manifold. A fourth flowmeter measured the mixture at the entrance of the combustion tube. Readings of the flowmeters may be used as an approximation to the gas composition. The temperature indicator was a Leeds & Northrup thermocouple potentiometer with an external galvanometer. The wattmeter was a Weston Model 310, scale 75–150 watts. The thermocouple metals were No. 36 platinum and platinum–10 per cent rhodium wire. The cold junction was immersed in an ice-water mixture contained in a Dewar flask.

Experiments on the type of catalyst were confined to platinum, quartz, and hopcalite. Hopcalite was found to be unsatisfactory. Quartz at 850° C. was found to be as effective as platinum in converting the hydrocarbons to carbon dioxide and water, but the rise in temperature attending the combustion with the former catalyst was only one-twentieth that of the latter. It was therefore felt that the thermal conductivity as well as the chemical stability were the more important properties of the catalyst. The oxide catalysts at 350° C. described by Yant and Hawk (*13*) were not used in the authors' work when it was found that platinum gave satisfactory results. Experiments on the variation of weight and length of platinum catalyst indicated that a tightly fitting platinum cylinder 4 cm. in length and filled with platinum scrap (total weight 4.25 grams) served to give adequate sensitivity to the temperature indicator. Thus a gas mixture containing 0.4 per cent methane, 4 per cent oxygen, and the balance nitrogen, produced a rise in temperature of 37° C. at a gas flow of 20 cc. per second. The temperature of the catalyst was 850° C. Since hydrogen and carbon monoxide burn more readily than the gaseous hydrocarbons, it was important that the gas mixture reach the metallic catalyst with no previous combustion. The catalytic mass must therefore be placed at the end of the furnace at which the gas mixture enters.

It is clear that secondary reactions must be avoided. The removal of sulfur dioxide and carbon dioxide would eliminate many possibilities. Extrapolation of the data of Nernst (*7*) indicated that a negligible amount of nitric oxide would be formed at 850° C. when air was passed over platinum. When the acidic oxides were removed, the composition of the synthetic flue gas striven for in the laboratory was 4 per cent oxygen, 0.3 to 1 per cent combustible, and the balance nitrogen. Inasmuch as the commercial gases containing hydrocarbons were not purified, the total carbon dioxide formed by combustion as previously described is reported as per cent methane and this amount when compared with the amount of carbon dioxide formed by contact with the catalyst gives the completeness of combustion. The illuminating gas had the

following percentage composition obtained by analysis: carbon dioxide, 2.15; unsaturates, 5.7; oxygen, 1.6; hydrogen, 39.0; carbon monoxide, 22.2; paraffins, 17.5. The heat of combustion (*12*) of the illuminating gas (450,000 joules) was estimated utilizing the following data: carbon monoxide determined by the iodine pentoxide method, carbon dioxide and shrinkage formed on combustion after removal of unsaturates, and carbon dioxide and shrinkage formed on total combustion.

Table IV. Relation between Rate of Gas Flow and Completeness of Combustion of Methane in Synthetic Flue Gas

(Platinum catalyst; temperature 850° C.; wattmeter readings to nearest 0.25 watt)

Rate	Composition of Gas[a] O_2	CH_4	Completeness of Combustion	Measured Watts	Calcd.[b] Watts	Ratio
Co./sec.	%	%	%			
20	4.2	0.25	90	4.0	1.6	2.5
26.5	5.4	0.5	90	8.0	4.3	1.9
32.5	4.6	0.55	95	10.0	6.2	1.6
43	3.3	1.05	95	17.75	15.7	1.1
46.5	4.7	0.5	70	8.0	5.9	1.3

[a] Balance nitrogen.
[b] Calculated, based on per cent combustion.

Sample calculation:

$$\frac{0.0025 \times 20 \times 890{,}160}{22{,}400 \times \frac{298}{273}} \times 0.9 = 1.6 \qquad \text{Ratio } \frac{4.0}{1.6} = 2.5$$

The experimental procedure found to work satisfactorily was to hold constant the wattage of the furnace and adjust the wattage of the auxiliary heater so that zero deflection in the thermocouple circuit was obtained when no combustible was present in the flowing gas and when the hot junction was at 850° C. When determining the heat value of a gas mixture (*10*), the change in the wattage of the auxiliary heater necessary to maintain zero deflection of the galvanometer in the thermocouple circuit was noted. The wattage of the auxiliary heater was maintained at a higher value than the anticipated watt-equivalent of the gas. The temperature at the external heater was approximately 1000° C., owing largely to radiation and the end effect.

In Table IV the rate of flow of the gas is compared with the completeness of the combustion. It is doubtful whether one can distinguish between 90 and 95 per cent. The column headed Ratio was obtained by comparing the measured change in watts in the auxiliary heater to the value obtained from the composition of the gas. This ratio should remain constant at a definite gas flow and be independent of the individual combustible compounds in the gas. The increased rate of flow of gas with its larger calorific content must be judiciously balanced with the completeness of combustion, in order that the maximum effect be obtained on the measuring instruments. Variations of 1 per cent in velocity (flowmeter reading) were shown to cause a 10 per cent error in the heat equivalent of the gas, when the rate of gas flow was approximately 20 cc. per second.

In Table V are compared the three different types of combustibles used in the experiments in order to illustrate the reproducibility of the apparatus. Some of the variations in the individual determinations are large and may be attributed, in part, to the fact that separate gas analyses were not made on each individual determination. Instead the readings of the flowmeter served to estimate the gas composition. A period of 3 to 4 minutes was required to obtain the maximum effect resulting from combustion. A comparison of the heat values of three types of combustible gas shows a good agreement when the uncertainty in the estimated heat of combustion of illuminating gas is considered. When the catalytic combustion method was compared with the procedure of flue-gas analysis described earlier in the paper on a sample of

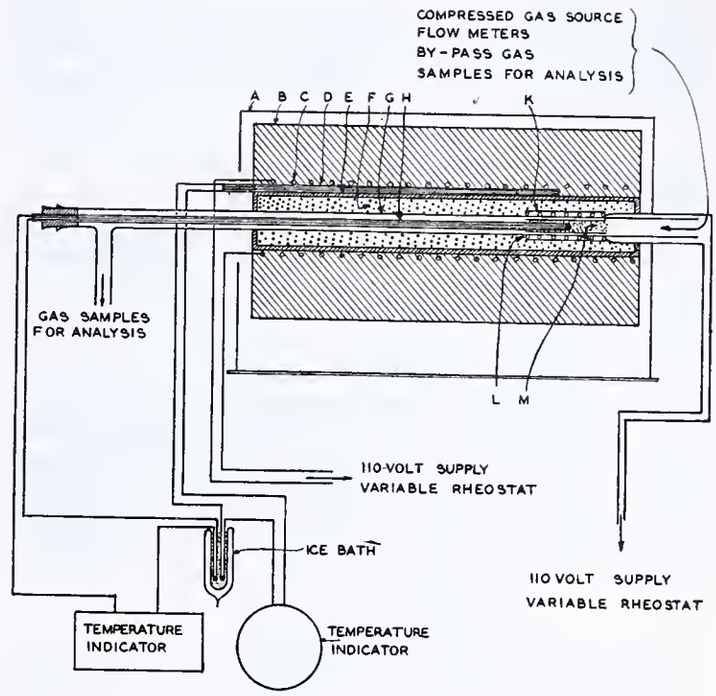

Figure 3. Apparatus for Direct Determination of Combustibles in Flue Gas

A. Aluminum box
B. External heater insulation
C. External heater
D. Quartz sheath for thermocouple, 2 mm. outside diameter
E. Quartz tube, 3-mm. wall, 22 mm. outside diameter
F. Asbestos fiber insulation
G. Quartz tube, 1.5-mm. wall, 8 mm. outside diameter
H. Quartz sheath, for platinum–platinum–rhodium thermocouple, 2 mm. outside diameter
K. Quartz tube, support for auxiliary heater
L. Auxiliary heater. No. 30 nichrome wire
M. Platinum cylinder and platinum chips (catalyst)

Table V. Calorific Content of Synthetic Flue Gas

(Temperature of platinum catalyst, 850° C. Rate of gas flow, 20 cc. per second. Complete combustion except for the first two methane (0.35 per cent) runs, which were 95 per cent complete. Wattmeter readings to nearest 0.25 watt. Gas composition 3.8 per cent oxygen, tabulated per cent combustibles, and balance nitrogen.)

	Measured Watts	Calcd.[a] Watts	Ratio	Comparison of Calorific Content of Synthetic Flue Gases[b]	Experimental	Calculated
0.35 Per Cent Methane						
	5.75					
	5.5					
	4.75					
	6.0			Hydrogen / Methane : $\frac{3.6}{2 \times 5.4}$ = 0.33	$\frac{1.6}{5.1}$ = 0.31	
	5.0					
	5.5					
	5.5					
Av.	5.4	2.55	2.1			
0.7 Per Cent Hydrogen						
	4.25					
	4.25					
	3.25			Ill. gas / Methane : $\frac{4.2 \times \frac{0.7}{0.54}}{2 \times 5.4}$ = 0.5	$\frac{2.6}{5.1}$ = 0.51	
	3.25					
	3.0					
Av.	3.6	1.6	2.2			
0.27 Per Cent Illuminating Gas						
	2.25					
	2.25					
	2.25					
	2.25					
Av.	2.25	1.0	2.2			
0.54 Per Cent Illuminating Gas						
	4.25					
	4.25					
	4.25					
	4.0					
Av.	4.2	2.0	2.1			

[a] The molal heats of combustion (*3*) in joules used in the calculations were methane, 890,160; hydrogen, 284,850; carbon monoxide, 282,890.
[b] Contained methane, hydrogen, or illuminating gas.

gas containing 0.54 per cent illuminating gas (Table V), the following results were obtained (it is assumed that 3 carbon monoxide = 3 hydrogen = 1 hydrocarbon for the approximate heat calculations):

	%	
Carbon monoxide	0.12	
Carbon dioxide (total)	0.28	
Shrinkage	0.75	
Hydrogen estimation		
Assume: $\frac{\text{shrinkage}}{\text{carbon dioxide}} = 1$	0.35	Revised calcd. watts (Table V)
Total combustible in terms of hydrogen	0.95	2.2
Assume: $\frac{\text{shrinkage}}{\text{carbon dioxide}} = 2$	0.25	
Total combustible in terms of hydrogen	0.85	2.0

In conclusion, it is obvious that the outlined procedures for gas analysis, because of the assumptions involved, find application only when the gas sample contains a small percentage of combustible. The results obtained in flue-gas analysis possess an accuracy satisfactory for use in estimating the combustible gas stack loss in steam-generator efficiency tests.

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Volumetric Microdetermination of Chloride and Potassium Ions

Application of the Potassium Method to Sea Water

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A NUMBER of years ago it became desirable to develop a simple titrimetric halide method for use in routine class work. The easy and sensitive adsorption indicator method of Fajans and co-workers (*2*, *3*) seemed to offer every possibility of easy adaptation to the microscale. The best indicator for this purpose seemed to be dichlorofluorescein, originally introduced by Kolthoff, Lauer, and Sunde (*9*). One of the authors (P.L.K.) accordingly made a study of the use of this indicator in titrations of small amounts of halide ion (0.2 to 0.5 mg. in samples of about 1 ml.). By introducing a few improvements into the macromethod as originally given (*9*), an entirely satisfactory micromethod was evolved. It seemed possible to adapt this method to the determination of potassium through titration of the chloride in the precipitate of potassium chloroplatinate. Since the standard chloroplatinate method, which is one of the most dependable methods for determination of potassium, is gravimetric, a considerable simplification would be introduced.

The alternatives to the chloroplatinate method for potassium are not free of objection. The perchlorate method is also gravimetric and is subject to difficulty on account of the rather high solubility of the potassium perchlorate. The cobaltinitrite method with its various modifications (*4*, *10*, *12*, *15*) is always subject to the use of an unstable reagent and the difficulty of obtaining a precipitate of constant known composition.

An easy and entirely satisfactory method for the determination of potassium in any medium to which the standard chloroplatinate method is applicable was accordingly developed. It depended on the reduction of the platinum in the precipitate to the metallic state by use of metallic magnesium in neutral solution, and the titration of the chloride released with silver nitrate, using dichlorofluorescein as indicator. In addition to the obvious advantage of being volumetric, there is a threefold factor relating the chloride to the potassium in the precipitate.

Experimental

Chloride Determination: For test purposes, pure potassium chloride solution was used for analysis. The samples were of the order of 1 ml. of 0.01 *N* solution, titrated directly with 0.005 *N* silver nitrate solution, using a 10-ml. buret calibrated in 0.02-ml. divisions. The sample was conveniently contained in the cut-off end of a test tube. The conditions under which a visible end point with dichlorofluorescein was obtained were: The solution had to be approximately neutral; the amount of indicator could not exceed 2 drops of 0.01 per cent solution of dichlorofluorescein; acetone had to be added in amounts approximating the original volume of the sample; and illumination had to be from the side or rear of the observer, instead of being in the rear of the sample as is customary.

The reaction of the sample could be assured by observation of the indicator itself. At the correct reaction the indicator was greenish and fluorescent and, if this was not the case, acid or base was added. Too much indicator definitely obscured the end point, too small a fraction being adsorbed on the precipitate. The titration was best performed in a partially darkened room by the light of a daylight lamp placed at the side of the observer. A black background was preferable to a white one. The addition of acetone to the solution was found to be absolutely necessary with the samples used. Alcohol was an aid, but was definitely inferior to acetone. The effect was in all probability on the dis-

persion of the precipitate, a point which may be critical in view of the small amount of total precipitate and the fact that the color change occurs on this, rather than in the solution. When the titration was carried out in this manner, the end point was sufficiently visible and extremely sharp and reproducible. Table I gives the results of the study of this titration.

TABLE I. RESULTS OF TITRATION

0.0100 *N* Potassium Chloride Sample	Acetone	0.00503 *N* Silver Nitrate Titer	Calculated
Ml.	Ml.	Ml.	Ml.
1.00	0	Indistinct end point	1.99
1.00	0	2.1 (approx.)	1.99
1.00	1	2.00	1.99
1.00	2	1.99	1.99
1.00	2	2.00	1.99
1.00	2	1.99	1.99
1.00	3	1.99	1.99
0.50	1	1.02	0.995
0.50	2	1.005	0.995
0.50	2	1.00	0.995
2.00	3	3.97	3.98
2.00	3	3.98	3.98

Table I indicates that the amount of acetone is not critical, but that its presence is necessary if the end point is to be distinct. This method has been in use in routine class work on simple solutions and certain biological materials for a period of some years and has amply demonstrated its reliability and ease. Interference by other ions is rare, except in the case of considerable amounts of phosphate, which definitely obscures the end point. Experience has shown it to be dependable in the determination of chloride, bromide, and iodide ions in combination with cations of all valences and types. The reproducibility and accuracy of this titration on the microscale is far superior to that obtained with the micro-Volhard or Mohr titrations, and the method is considerably more rapid than the Volhard titration.

POTASSIUM DETERMINATION: For preliminary testing of the method, samples of about 1 or 2 ml. of 0.01 or 0.005 *N* potassium chloride solution were used. Later, sea-water samples of 1 or 2 ml. were used to test the applicability of the method to solutions of high and varied salt content. The general method which gave satisfactory results with the sea-water samples is given below.

The sample was pipetted into a small porcelain crucible having a capacity of about 10 ml. Excess chloroplatinic acid solution (1 ml. of a solution containing 0.5 per cent platinum) was added and the solution evaporated to dryness on a steam bath. The general method of washing, which was applicable both to simple solutions and to sea water, was as follows:

Two successive 1-ml. portions of 80 per cent alcohol saturated with potassium chloroplatinate were used, followed by two or three similar portions of 20 per cent ammonium chloride, which had been shaken with potassium chloroplatinate, followed by three or four similar washings with the 80 per cent alcohol used previously. The final washing with alcohol was primarily for removal of the ammonium chloride, and the completeness of this removal was checked by observing whether a crust of ammonium chloride formed on the filter when the alcohol evaporated. With simple potassium solutions less careful washing could be used without affecting the results.

The precipitate, along with any asbestos which was used on the filter, was washed back into the crucible with 1 or 2 ml. of hot water. A small amount of powdered metallic magnesium was added to the neutral solution, and the mixture again evaporated to dryness on the water bath. When dry, a known amount of water, usually 3 ml., was added to dissolve the chlorides and the mixture filtered through a small dry filter paper. The chloride in an aliquot of the filtrate, usually 1 ml., was titrated with 0.005 *N* silver nitrate from a 10-ml. buret as described above, using dichlorofluorescein as indicator.

The filtration of the potassium chloroplatinate was the only point of technic that called for special consideration. While any small asbestos or sintered-glass filter could be adapted to this purpose, it was found that a filter stick of sintered glass was by far the most convenient. Such a filter has been described by Kirk (*6*), with a method of manufacture by Kirk, Craig, and Rosenfels (*7*). It has been found far simpler and almost equally satisfactory to prepare a somewhat coarser grade of sintered-glass filter stick by the method described by Kirk (*5*). These filter sticks were mounted in a battery of six, which could be raised and lowered individually or collectively, thus making possible any number of simultaneous filtrations up to the number of filter sticks so mounted. Asbestos was used over the ends by simply sucking a layer of it on the filter from a flask of suspended shreds in water, as described by Miller and Kirk (*11*). The type of filter stick described by Emich (*1*) was not tried, but could probably have been used. The filter described by Kirk and Schmidt (*8*) was used satisfactorily, but was somewhat slower and less convenient than the sintered glass filter stick.

The calculation of the data involves the factor to correct for the aliquot and an atomic ratio of 1 to 3 which relates the potassium to the chloride in the precipitate. Table II gives the results of a series of determinations of potassium in potassium chloride solutions.

TABLE II. POTASSIUM DETERMINATION IN POTASSIUM CHLORIDE SOLUTIONS

Sample		Titer 0.00496 *N* Silver Nitrate	Calculated Potassium Found		Error
Ml.	Normality	Ml.	Mg.	Mg.	Mg
Aliquot, 0.983 Ml. from 2.906 Ml.					
0.983	0.0100	2.00	0.384	0.383	−0.001
0.983	0.0100	2.01	0.384	0.384	0
0.983	0.0100	1.99	0.384	0.381	−0.003
0.983	0.0100	1.98	0.384	0.378	−0.006
0.983	0.0100	1.98	0.384	0.378	−0.006
0.983	0.0100	1.99	0.384	0.381	−0.003
0.983	0.0100	2.01	0.384	0.384	0
Aliquot, 0.983 Ml. from 5.812 Ml.					
1.966	0.0100	2.00	0.768	0.765	−0.003
1.966	0.0100	2.00	0.768	0.765	−0.003
1.966	0.0100	1.99	0.768	0.764	−0.004
Aliquot, 1.999 Ml. from 2.906 Ml.					
0.983	0.0051	2.10	0.196	0.198	+0.002
0.983	0.0051	2.07	0.196	0.195	−0.001
0.983	0.0051	2.12	0.196	0.199	+0.003

Sea water was chosen as a material on which to check the applicability of this method to mixed salt solutions, since the content of potassium is low, while that of other salts, particularly those of sodium, is high. The results of this study are shown in Table III.

TABLE III. POTASSIUM DETERMINATION IN SEA WATER

Sample	Potassium in Original Sea Water Sample	Deviation from Mean
Ml. of Sea Water	Mg./Ml.	Mg.
0.983	0.342	−0.002
0.983	0.344	0
0.983	0.344	0
0.983	0.346	+0.002
0.983	0.344	0
1.97	0.342	−0.002
1.97	0.342	−0.002
1.97	0.344	0
1.97	0.346	+0.002
1.97	0.344	0
0.983 + 0.397 mg. added potassium	0.343	−0.001
0.983 + 0.397 mg. added potassium	0.346	+0.002
0.983 + 0.397 mg. added potassium	0.341	−0.003
0.983 + 0.397 mg. added potassium	0.341	−0.003
0.983 + 0.397 mg. added potassium	0.346	+0.002
	Mean 0.344	

The reduction of potassium chloroplatinate to chloride and platinum with metallic magnesium in neutral solution had several advantages: The excess magnesium could be filtered off after reduction, thus avoiding later complications due to reduction of silver ion used in titration; magnesium effectively reduced the chloroplatinate in a neutral solution, thus avoiding any neutralization before titration; and the magnesium ion formed during the process had no effect upon the chloride titration. The use of formaldehyde for reduction was attempted, but it was found that a condensation

product resulted which could be removed only by the use of considerable amounts of hydrogen peroxide and boiling.

Whereas the use of alcohol saturated with potassium chloroplatinate is rather general, this is a particularly necessary precaution with small amounts of precipitate. When alcohol of any strength was used without this preliminary saturation, low results invariably resulted. Eighty per cent alcohol, saturated with potassium chloroplatinate, was used because of the greater solubility of sodium salts in this strength than in stronger alcohol solutions (*14*). It should also be noted that any aldehyde or acetic acid, which are common contaminants of alcohol, may produce some reduction of the chloroplatinate, giving low results (*13*).

It is apparent that this procedure will be satisfactory in any case in which the gravimetric chloroplatinate method may be used. This volumetric modification is rapid, simple in operation, and appears to yield on small samples an accuracy which is superior to that which would be obtained gravimetrically, since the deviations are not greater than would be expected from ordinary weighing deviations on the microbalance.

Further work is in progress on the application of these methods to biological fluids.

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Analysis of *n*-Butanol, Acetone, and Ethanol in Aqueous Solution

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In the butyl-acetonic fermentation of corn mash and other suitable substrates, *n*-butanol, acetone, and ethanol are produced in the ratio of about 6 to 3 to 1. Hydrogen, carbon dioxide, acetic acid, butyric acid, and acetylmethylcarbinol are also formed, but the yield and proportion of the three solvents are of particular interest. It becomes necessary, therefore, in laboratory research on this process, to have available a rapid routine method for measuring these products. The method should also be applicable when only small amounts of the materials are available.

Reilly and Ralph (*6*) have reported the densities of the aqueous solutions of the three solvents. Bogin (*1*) developed a quantitative method based upon the determination of the total concentration of the three in the aqueous distillate, the measurement of the acetone by the usual iodometric method, and the determination of the *n*-butanol–ethanol ratio by titration of the anhydrous alcohols with water.

Werkman and Osburn (*7*) developed a procedure for the analysis of solutions of *n*-butanol and ethanol, based upon their oxidation with potassium dichromate and phosphoric acid, the acetone having been previously removed with 2,4-dinitrophenylhydrazine. The butanol yielded 90.7 per cent butyric acid and 9.3 per cent acetic acid, while the ethanol yielded only acetic acid. The acid ratio was determined by partitioning with isopropyl ether. Johnson (*5*) used a similar method, except that he measured the acid ratio by a modified Duclaux procedure. Fang (*2*) developed a method based upon measurement of the refractive index, determination of acetone by the usual iodometric method, and a second measurement of refractive index after partition with carbon tetrachloride, which removed *n*-butanol to a considerably greater extent than it did the acetone or ethanol.

Several methods have been used in these laboratories for the analysis of the two alcohols and, as a result, procedures have been developed for their determination which have met all requirements for speed, simplicity, and accuracy. They have been thoroughly checked by a number of individuals and found to be well suited for routine use.

The fermentation mixture, representing a known weight of substrate, is neutralized to pH 7.0 to 7.5, and about one-third is carefully distilled into a receiver submerged in cold water. Usually 100 cc. of distillate are thus collected. All calculations are then based upon this volume of distillate. If it is of interest to estimate only the total solvent yield, the specific gravity, 25°/25°, is measured and the solvent concentration calculated by means of Equation 1. This equation holds for a 6 to 3 to 1 ratio, but is inaccurate when the ratio varies appreciably from the above proportion. The total concentration should not exceed about 10 grams per 100 cc. and is usually kept below 5 grams per 100 cc.

$$\text{Total solvents, grams/100 cc.} = (1.0000 - \text{sp. gr. } 25°/25°)\ 698 \quad (1)$$

The dipping refractometer may also be used to measure the total solvent concentration. The reading, 25°/25°, is expressed by Equation 2, in which R is the dipping refractometer reading and B, A, and E are the concentration of *n*-butanol, acetone, and ethanol, respectively, in grams per 100 cc. With a ratio of 6 to 3 to 1, the total solvent concentration is given by Equation 3.

$$R = 13.25 + 2.646B + 1.800A + 1.610E \quad (2)$$

$$\text{Total solvents, grams/100 cc.} = 0.437\ (R - 13.25) \quad (3)$$

When it is desired to separate and identify the products, sufficient distillate to yield about 200 cc. of anhydrous solvents is saturated with sodium chloride, about one-fourth distilled into a cold receiver, and saturated with anhydrous potassium carbonate. The solvents separating are further

dried with anhydrous potassium carbonate and carefully fractionated. The usual derivatives can then be prepared. If no other compounds than *n*-butanol, acetone, and ethanol are present, and this is ordinarily the case, the procedures described below may be applied.

The data presented were obtained by the use of aqueous systems of the highly purified solvents.

The acetone is determined by the Goodwin (*4*) modification of the Messenger method. The interference from ethanol is negligible, unless it be present in much larger amounts than is the acetone. One gram of acetone consumes as much iodine as 100 grams of ethanol under the conditions employed in the analysis.

Determination of Ethanol and *n*-Butanol

When a mixture of *n*-butanol, acetone, and ethanol is oxidized with potassium dichromate and sulfuric acid, the reducing value of the solution depends upon the concentration of sulfuric acid, time, and temperature, as shown by Fauser (*3*). He found that 10 minutes' exposure of a 30- to 40-cc. mixture in a 2.5 × 25 cm. test tube in a boiling water bath gave easily duplicated results if the sulfuric acid concentration was carefully adjusted. Two flat portions were observed in the curve when reducing value was plotted against acid concentration, one when 10 volumes of acid per 30 cc. of mixture were used, and the second when 40 cc. of mixture contained 25 cc. of concentrated sulfuric acid. The difference between the reducing values obtained under these different conditions was found to be due entirely to the *n*-butanol and acetone. The procedure for the determination of the alcohols is as follows:

Ten cubic centimeters of original distillate containing not more than 5 grams of alcohols are diluted to 100 cc. and 10 cc. of this dilution are added to a cold mixture of 10 cc. of 0.4 *N* potassium dichromate and 10 cc. of concentrated sulfuric acid in a 2.5 by 25 cm. test tube. Two glass rods are dropped into the tube and the contents thoroughly mixed. A stopper carrying a 1-mm. capillary tube, the lower end of which is bent at right angles, is inserted and the tube placed in a vigorously boiling water bath. After 10 minutes' exposure, it is cooled and diluted to 400 cc. in a 1-liter Erlenmeyer flask. Fifteen cubic centimeters of a 20 per cent potassium iodide solution are then added, the flask is stoppered and allowed to stand 2 minutes, and the iodine released is titrated with 0.1 *N* sodium thiosulfate. A blank is run in the same way. The difference is designated as M_1 and has a value shown by Equation 4, in which M_1 is in cubic centimeters of 0.1000 *N* dichromate consumed, *B* is equal to the weight, in grams, of butanol in the original distillate, *A*, the acetone, and *E*, the ethanol, on the same basis.

$$M_1 = 6.92\,B + 0.691\,A + 8.78\,E \qquad (4)$$

A second titration is made to obtain another equation, and one of two procedures may be used. In one, a second oxidation, exactly like the above, is applied to a sample of distillate extracted with carbon tetrachloride. Twenty cubic centimeters of the distillate are placed in a test tube with 40 cc. of carbon tetrachloride, shaken, and allowed to stand 2 hours at 25° C. It is essential that the temperature be closely controlled. Ten cubic centimeters of the aqueous solution are removed, diluted to 100 cc. and 10 cc. of this dilution oxidized as above, to obtain a value, M_2, which is represented by Equation 5.

$$M_2 = 2.75\,B + 0.386\,A + 8.22\,E \text{ plus correction} \qquad (5)$$

The extraction of butanol is not a linear function of concentration, and the correction represents the deviation from the linear relation assumed in applying the constant, 2.75. The terms have the dimensions used above.

Instead of extracting with carbon tetrachloride, a second equation may be obtained by carrying out the oxidation under different conditions. Ten cubic centimeters of original distillate, containing not more than 2 grams of alcohols per 100 cc., are diluted to 100 cc., and 5 cc. of this dilution are added to a cold mixture of 25 cc. of concentrated sulfuric acid and 10 cc. of 0.4 *N* potassium dichromate in a 2.5 by 25 cm. test tube and the procedure for M_1 is followed. A blank is run in the same way. The difference in titration is multiplied by two to give the value, *N*, shown in Equation 6, in which the dimensions are as above.

$$N = 24.62\,B + 17.68\,A + 8.84\,E \qquad (6)$$

From these values, ethanol and *n*-butanol may be calculated by means of Equations 7, 8, and 9.

$$B = 0.25\,(M_1 - M_2) - 0.01\,M_2 - 0.07\,A + \text{correction (see Table II)} \qquad (7)$$

$$B = 0.057\,(N - M_1) - 0.96\,A \qquad (8)$$

$$E = 0.114\,M_1 - 0.788\,B - 0.0787\,A \qquad (9)$$

In Table I are given data showing the application of the above equations to various mixtures of the pure solvents. The use of these relations is not confined to mixtures, for they are equally applicable to the solvents alone.

Table I. Estimation of Butyl and Ethyl Alcohol in Mixtures with Acetone

Solvents in Original Distillate, G./100 Cc.					BuOH Found, G./100 Cc.		EtOH Found, G./100 Cc.	
BuOH	Me_2CO	EtOH	M_1	M_2	Calc.	Error	Calc.	Error
By Oxidation-Extraction Method								
3.81	0.87	0.88	34.0	18.0	3.81	±0.00	0.81	−0.07
3.52	0.87	1.07	34.3	19.8	3.50	−0.02	1.06	−0.01
3.52	1.72	0.29	26.7	12.1	3.53	+0.01	0.22	−0.07
4.32	1.08	0.29	32.4	14.0	4.27	−0.05	0.22	−0.07
0.59	0.21	0.10	4.9	2.7	0.59	±0.00	0.08	−0.02
1.17	0.43	0.19	9.9	5.4	1.18	+0.01	0.18	−0.01
1.76	0.64	0.29	15.0	8.1	1.71	−0.05	0.27	−0.02
2.35	0.86	0.39	19.7	10.6	2.33	−0.02	0.32	−0.07
2.93	1.07	0.48	25.0	13.2	2.96	+0.03	0.46	−0.02
3.09	1.29	1.07	31.7	18.9	3.11	+0.02	1.07	±0.00
4.32	1.29	0.00	30.1	11.6	4.29	−0.03	−0.06	−0.06
0.00	1.72	1.17	11.2	10.2	−0.02	−0.02	1.15	−0.02
By Double-Oxidation Method								
1.50	0.75	0.30	13.4	52.2	1.49	−0.01	0.29	−0.01
0.80	1.00	0.40	9.5	40.6	0.81	+0.01	0.37	−0.03
0.40	1.00	0.40	6.7	30.9	0.42	+0.02	0.37	−0.03
1.50	0.90	0.30	13.5	54.7	1.48	−0.02	0.29	−0.01
1.50	0.60	0.30	13.4	49.6	1.48	−0.02	0.30	±0.00
1.00	0.50	1.00	13.2	39.0	0.99	−0.01	0.99	−0.01
1.00	0.50	0.50	11.6	37.6	1.00	±0.00	0.49	−0.01
1.00	0.50	0.40	10.7	37.0	1.02	+0.02	0.39	−0.01
1.00	1.00	1.00	16.2	50.7	1.00	±0.00	0.97	−0.03
0.24	0.11	0.04	2.1	7.8	0.22	−0.02	0.04	±0.00
0.41	0.15	0.00	10.2	37.6	1.42	+0.01	0.05	+0.05
1.25	0.00	0.30	11.6	33.9	1.27	+0.02	0.33	+0.03

Summary

Methods suitable for the rapid routine analysis of aqueous solutions of *n*-butanol, acetone, and ethanol are described. Acetone is measured by an iodometric method and the alcohols are measured by oxidation with dichromate and extraction with carbon tetrachloride, or by oxidation at two different concentrations of sulfuric acid in the oxidizing mixture. The methods are equally accurate and rapid. For purposes of checking, a combination of the methods may be employed. As a means of proving the identity of the prod-

Table II. Standard Corrections for Equation 4

BuOH Uncorrected G./100 Cc.	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0	+0.02	+0.04	+0.06	+0.08	+0.10	+0.12	+0.14	+0.16	+0.18
1	+0.19	+0.21	+0.22	+0.24	+0.25	+0.26	+0.27	+0.28	+0.29	+0.30
2	+0.31	+0.32	+0.32	+0.33	+0.33	+0.33	+0.33	+0.33	+0.32	+0.31
3	+0.31	+0.30	+0.28	+0.27	+0.25	+0.23	+0.21	+0.19	+0.17	+0.14
4	+0.12	+0.10	+0.07	+0.05	+0.02	±0.00	−0.03	−0.06	−0.09	−0.11
5	−0.14	−0.16	−0.18	−0.21	−0.23	−0.26	−0.28	−0.31	−0.33	−0.36
6	−0.39	−0.42	−0.44	−0.46	−0.49	−0.52	−0.54	−0.57	−0.59	−0.61

ucts, both the oxidation and the oxidation-extraction methods, taken in conjunction with measurement of specific gravity and the dipping refractometer reading, will prove of value.

Acknowledgment

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Estimation of Small Amounts of Lead in Copper

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LEAD occurs in most refined copper in about the same amount as other metallic impurities, from a few to several hundred parts per million. Several methods have been proposed for its separation and estimation. Heath (*1*) and Jones (*2*) separate lead as dioxide by electrolyzing a nitric acid solution of the copper. Keffer (*3*) separates the lead by co-precipitation with calcium carbonate from an ammoniacal solution before electrolysis. Electrolytic methods for lead are open to criticism because some of the lead is apt to deposit with the copper; other elements, such as bismuth and manganese, may deposit with the lead; the composition of the deposited lead peroxide varies; and prevention of mechanical loss while handling the deposit is difficult.

In order to find a better method for the separation of lead from copper the authors have tried a number of schemes, all based on the formation of an insoluble lead salt and its collection by some occluding agent. The method adopted proved capable of separating and estimating, with an error of about 50 per cent, as little as one part of lead in one million parts of copper.

Purification of Reagents

Nitric, hydrochloric, and acetic acids and ammonium hydroxide were tested for lead by distilling 500 cc. of each from a silica still, dissolving the residue in distilled nitric acid, concentrating to 5 cc., and then testing the concentrate spectrographically. These reagents were lead-free.

Solutions of manganese sulfate (25 per cent), ferrous ammonium sulfate (20 per cent), calcium chloride (20 per cent), and disodium hydrogen phosphate (50 per cent) were rendered lead-free by adding a few cubic centimeters of a saturated solution of lead-free copper sulfate, saturating with hydrogen sulfide, filtering off the precipitated sulfides, and repeating until a precipitate was obtained which showed no spectrographic trace of lead. Usually the third precipitate was lead-free.

Ten per cent potassium dichromate solution was treated with a little of the lead-free ferrous ammonium sulfate solution, ammonium hydroxide was added, and the mixed precipitate of iron and chromium hydroxides was filtered out and tested. This procedure was repeated until the precipitate gave no test for lead.

Five per cent potassium permanganate solution was treated with a little of the lead-free dichromate solution and then repeatedly with ferrous ammonium sulfate and ammonium hydroxide until a lead-free precipitate was obtained.

The authors were unable to remove the rather large amount of lead present in the c. p. reagent brand of ammonium carbonate. Lead-free ammonium carbonate solution was prepared by passing carbon dioxide into a solution of two parts of water to one part of strong ammonium hydroxide until a precipitate formed.

Table I gives a summary of the various schemes of separation which were tried. In each case 50 grams of copper containing about 0.5 mg. of lead were washed in hydrochloric acid to remove surface impurities and dissolved in 200 cc. of nitric acid. From this point the procedure varied.

Procedure

1. The sample was taken to fumes with sulfuric acid, diluted to 500 cc., and heated to boiling and then 2 cc. of manganese sulfate solution were added. Ten cubic centimeters of permanganate solution were added with constant stirring and the solution was allowed to stand overnight. The precipitate was dissolved and reprecipitated as PbS, which was then dissolved in nitric acid and tested spectroscopically for lead.
2. Ammonium hydroxide was added to neutralize the excess nitric acid, the solution was diluted to 500 cc., and 15 cc. of acetic acid were added. The pH of the solution at this point, determined by means of a quinhydrone electrode, was 2.0. Ten cubic centimeters of the dichromate solution were added and then the manganese dioxide precipitation was carried out as described under (1). Each of three consecutive precipitates showed a small amount of lead.
3. The excess nitric acid was boiled off, 15 grams of borax were added, and the solution was diluted to 500 cc. The pH was 2.8. Three manganese dioxide precipitates, after the addition of dichromate solution, failed to remove all of the lead.
4. The solution was prepared as in (3), but 25 cc. of ferrous ammonium sulfate were added instead of the manganese sulfate and permanganate. Three consecutive precipitations all showed lead.
5. Four grams of Norite were added to a solution prepared as in (3) and the mixture was stirred mechanically overnight. The Norite was filtered out and extracted with hot nitric acid. This procedure failed to remove any lead from the solution.
6. The nitric acid solution was diluted to 500 cc., and then 10 cc. of dichromate solution, 25 cc. of ferrous ammonium sulfate solution, and enough ammonium hydroxide to bring down a small amount of copper hydroxide were added. Next 200 cc. of concentrated ammonium hydroxide were added and the solution was heated to 80° C. and filtered hot. Three consecutive precipitates all showed a small amount of lead.
7. This procedure was the same as (6), except that 3 cc. of manganese sulfate and 10 cc. of permanganate solutions were substituted for the iron. A complete separation was not obtained.
8. To the hot ammoniacal solution containing dichromate 4 grams of Norite were added. After a few hours of stirring the Norite was filtered out and extracted with nitric acid. No lead was removed by this method.
9. To the cold ammoniacal solution were added 50 cc. of ammonium carbonate solution, followed by 5 cc. of calcium chloride solution. It was found that if the calcium chloride was added before the ammonium carbonate (method of Keffer, *3*) a much less efficient separation was made. The mixture was stirred well and allowed to stand overnight, and the precipitate filtered out and tested in the usual way. Although this procedure gave a better separation than any of those previously mentioned, it was unsatisfactory. Three consecutive precipitates all showed lead.

Table I. Separation of Small Amounts of Lead from Copper

	Nature of Solution	Insoluble Lead Salt	Collector	Result
1	H_2SO_4	$PbSO_4$	MnO_2	Unsatisfactory
2	HNO_3 + HOAc (pH 2.0)	$PbCrO_4$	MnO_2	Unsatisfactory
3	HNO_3 + Na_2B_4O (pH 2.8)	$PbCrO_4$	MnO_2	Unsatisfactory
4	HNO_3 + Na_2B_4O (pH 2.8)	$PbCrO_4$	$Fe(OH)_3$	Unsatisfactory
5	HNO_3 + Na_2B_4O (pH 2.8)	$PbCrO_4$	Norite	Unsatisfactory
6	NH_4OH	$PbCrO_4$	$Fe(OH)_3$	Unsatisfactory
7	NH_4OH	$PbCrO_4$	$MnO(OH)_2$	Unsatisfactory
8	NH_4OH	$PbCrO_4$	Norite	Unsatisfactory
9	NH_4OH	$PbCO_3$	$CaCO_3$	Unsatisfactory
10	NH_4OH	$Pb_3(PO_4)_2$	$Ca_3(PO_4)_2$ + $CaCO_3$	Satisfactory

Table II. Separation of Lead in Copper

Sample	% Lead	Sample	% Lead
1	0.0010	8	0.0010
2	0.0008	9	0.0008
3	0.0007	10	0.0020
4	0.0060	11	0.0005
5	0.0011	12	0.0007
6	0.0008	13	0.0010
7	0.0010	14	0.0008

10. This method was used in all subsequent work, and will therefore be described in detail. A 50-gram sample of copper was washed with hot concentrated hydrochloric acid, followed by distilled water, and dissolved in 200 cc. of concentrated nitric acid. The brown fumes were boiled off, and 1200 cc. of water and 350 cc. of concentrated ammonium hydroxide were added. Then 2 cc. of disodium phosphate and 50 cc. of ammonium carbonate solutions were added, the solution was mixed well, and 25 cc. of calcium chloride solution added all at once with stirring. After standing overnight it was filtered through a No. 4 Jena glass crucible. The precipitate was dissolved in 25 cc. of hydrochloric acid, neutralized with ammonium hydroxide, then acidified with a few drops of acid and saturated with hydrogen sulfide before filtering. The sulfides were dissolved in nitric acid and concentrated to 5 cc. All the lead is separated by this method. A second precipitation showed no trace. Two milligrams of lead were added to this lead-free copper solution and a third precipitation was made. This contained the 2 mg. A fourth precipitate again showed no lead.

A number of samples of refined copper from various sources were subjected to this method. The results obtained by comparison of their spectrograms with those of standards taken on the same plate, according to the method of Nitchie (*4*), are given in Table II.

Preparation of Standards

Solution A. Three grams of lead-free copper were dissolved in 300 cc. of nitric acid.

Solution B. One gram of test lead was dissolved in a little nitric acid and diluted to one liter.

Four cubic centimeters of B and 6 cc. of A were mixed. Then 5 cc. of the mixture were mixed with 5 cc. of A to give the second standard, and 5 cc. of the second standard were mixed with 5 cc. of A to give the third standard. In this way nine standards were prepared with the following concentrations: 2, 1, 0.5, 0.25, 0.125, 0.0625, 0.0312, 0.0156, and 0.0078 mg. per 5 cc.

When 0.1 cc. of each of the standards was dried on a graphite electrode and arced, the lead line at 2833 Å. graded nicely in intensity and was visible in the first seven. The smallest amount of lead detectable by this method and by the particular Gartner Littrow-type spectrograph used in this work was therefore 6×10^{-7} gram.

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Detection and Volumetric Estimation of Alkali Metals

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It is sometimes not easy to decide by means of common reagents whether or not the alkalinity of an ash is due to alkali metal. For example, an ash from a mixed base grease containing calcium and sodium presents somewhat the same flaky appearance as an ash from a calcium soap grease. The usual flame test is uncertain in this case.

Soap Formation as a Test

The qualitative test here outlined makes use of the insolubility of alkaline-earth oleates and the solubility of alkali oleate in water.

A portion of the hot, aqueous, filtered extract of the alkaline ash is added with shaking to a hot alcoholic solution of oleic acid until the mixture is alkaline to phenolphthalein. The alcoholic strength must be kept above 50 per cent at all times to prevent hydrolysis of the soap formed. The solution is evaporated on the steam bath with a current of air blowing into the flask until the odor of alcohol is very faint. Five volumes of distilled water are added to the aqueous residue, the solution is warmed and shaken, and any alkaline-earth soaps are filtered off. The filtrate is examined for ability to froth on shaking, and tested for alkali soap by the addition of barium chloride solution. A white, curdy precipitate confirms alkalinity due to alkali metal in the ash. A faintly opalescent filtrate that does not froth, nor increase in cloudiness upon the addition of barium chloride, is sometimes encountered when alkaline earth compounds alone are present. It should not be confused with the soapy frothy filtrate, yielding a precipitate with barium chloride, due to alkali soaps.

This test has the advantage of preferentially detecting alkalinity due to sodium or potassium, not showing sodium or potassium that may be also present in neutral combination as chlorides or sulfates. Other sodium or potassium reagents give information only as to the total content of these metals. This test is particularly adapted to distinguish sodium and potassium from calcium in the ash of lubricating greases.

Quantitative Volumetric Determination

The quantitative estimation was designed primarily as a fairly rapid method for alkali metals in the ash obtained by the ignition of petroleum products and compounds. It has been extended to the determination of these metals in their sulfates, to which form many other of their salts can be easily converted.

It is applied in the cases cited by treating the ash or salt with concentrated sulfuric acid, and decomposing the excess sulfuric acid and heavy metal sulfates by heating carefully until no more sulfur trioxide fumes are given off.

Table I. Results on Known Mixtures

Mixture	Weight of Sample	Sodium Carbonate In mixture	Sodium Carbonate Found	Sodium In mixture	Sodium Found
	Grams	%	%	%	%
Ammonium sulfate, calcium hydroxide,	0.176	35.2	35.2	15.3	15.3
and sodium carbonate	0.240	37.1	37.2	16.1	16.2
Fused sodium chloride	0.366	..	..	39.4	39.1
	0.146	..	..	..	40.0
				Potassium	
Potassium nitrate	0.406	..	..	38.6	38.6
	0.230	..	..	..	38.5

The sulfated residue is dissolved as far as possible in water. Solid barium hydroxide is added in excess to precipitate sulfates as barium sulfate, and to convert sodium and/or potassium sulfate to the hydroxide.

$$Na_2SO_4 + Ba(OH)_2 \longrightarrow 2NaOH + BaSO_4\downarrow$$

The precipitate, which may include other undissolved alkaline-earth sulfates, is filtered off and washed well with hot water, and ammonium carbonate is added to the boiling combined filtrate and washings to precipitate soluble alkaline-earth compounds as carbonates. The carbonates are filtered off, washed well with hot water, and the filtrate is boiled down to one-fifth of its volume to decompose and get rid of excess ammonium carbonate. (There should be no odor of ammonia at this point.) After cooling, any slight precipitate of alkaline-earth carbonates is filtered off, washed with water at room temperature, and the combined filtrate and washings are titrated to a methyl orange end point with 0.1 *N* acid in the usual manner. The acid consumed is calculated to per cent sodium or potassium, as the case may be. If they are both present, this titration would represent the total alkalinity due to alkali metals.

Since the estimation is based on getting the alkali metals in the form of soluble compounds, it is not necessary to burn off all carbon or ignite the ash to constant weight. This reduces the loss by volatility of alkali metal compounds, which is a troublesome factor in the usual gravimetric determinations of the alkali metals. It is hoped that this method may be useful in estimating alkali metals in other fields of analytical procedure.

Results on Unknown Mixtures

Neutrally bound alkali metals in the ash may be calculated from the difference between the result obtained by the method as outlined and the result obtained by determining the alkalinity of the ash to methyl orange. Results of tests on ash from soda-base grease, containing 0.93 per cent of total sulfur, showed the following:

Alkalinity of ash as sodium, uncorrected	30.8	30.9
Total sodium by this method, per cent	34.6	34.8
Neutrally bound sodium, per cent	3.8	3.8

Acknowledgment

The author wishes to thank Harry Levin and Karl Uhrig for helpful criticisms and suggestions.

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Detection of Benzene in Alcohol

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BENZENE may occur in alcohol in small amounts, and is undesirable in alcohol used for some purposes. The presence of benzene may be due to faulty process, or to accidental contamination. When the benzene content is too small for any of the turbidity tests with water, indications of its presence are usually obtained through taste and odor. Unfortunately, taste and odor tests do not give uniformly positive selective indications of the presence of benzene in low concentration. A direct and sensitive chemical test for small amounts of benzene in alcohol is therefore of value in the examination of alcohol.

A reliable method was desired for detecting benzene in concentrations of the order of 1 part by volume in 10,000, in alcohol of good quality otherwise. After unsatisfactory results by other methods a procedure involving concentration of the benzene by extraction, nitration of the extract, and color reaction of the nitration product was devised and applied with satisfactory results.

Reagents Required

Carbon tetrachloride, reagent grade.

Acetone, reagent grade.

Amyl alcohol (redistilled crude fusel oil) refluxed with strong caustic soda solution, and distilled from the alkali, collecting for use the dry fraction boiling at 128° to 132° C.

Nitrating acid: 70 grams of reagent 20 per cent oleum, 45 grams of reagent sulfuric acid of specific gravity 1.84, and 43 grams of reagent nitric acid of specific gravity 1.42.

Sodium sulfate solution, containing 10 grams of the anhydrous salt in 100 cc. of solution.

Caustic soda solution, 140 grams of reagent (sticks) made up to 250 cc. at room temperature.

Procedure

If the alcohol contains much above 0.01 per cent benzene by volume, as indicated by test on the undiluted sample, it is diluted to approximately that value with alcohol free from benzene. A 40-cc. portion is placed in a 100-cc. glass-stoppered cylinder with 6 cc. of carbon tetrachloride. Distilled water is added to the 90 cc. mark, followed by 10 cc. of sodium sulfate solution. The cylinder is stoppered, shaken thoroughly, and allowed to stand until the layers separate sharply. Five cubic centimeters of the bottom layer are transferred by pipet to a test tube. Three cubic centimeters of nitrating acid are measured in a small cylinder and added to the test tube, which is shaken carefully but thoroughly. During 10 minutes the tube is shaken twice more, and at the end of that time, 20 cc. of distilled water are added, preferably rapidly from a cylinder. After mixing by pouring into another test tube and back again, the bulk of the water layer is decanted and discarded. The lower layer with a small amount of water layer is placed in an evaporating dish on an electric hot plate. When the carbon tetrachloride is gone, the dish is emptied into the same test tube just used, and is rinsed into this tube with 1 cc. of amyl alcohol. The dish is then rinsed into the tube using 4 cc. of caustic soda solution. The tube is mixed by swirling and then 1 cc. of acetone is added, the tube is swirled again, and placed in a rack for observation of color produced in the top layer.

Indications

Pure benzene at the concentration 1 in 10,000 by volume in a rectified alcohol of ordinary purity gives by this test a red color with a purple quality in the top layer. This color holds for some hours, and finally fades to a dull orange-red. As the benzene content rises above 0.01 per cent, the color produced soon becomes too dark for identification, and dilution with alcohol free from benzene is necessary. Pure toluene gives a slightly brownish yellow and reagent xylene (chiefly *m*-xylene) produces a definite though not intense green, which fades in 30 minutes, giving way to a dull orange. Blank runs should always be run in duplicate with a test series; they give a light clear lemon yellow. Thorough cleaning of the apparatus between tests is necessary to maintain blank indications. Among other hydrocarbons tested, denaturing gasolines gave yellow colors of somewhat orange cast and a cer-

tain kerosene gave a reddish color, readily distinguished from the benzene color.

Precautions

If suitable concentration methods and adequate precautions are used, concentrations of benzene well below 1 in 10,000 should be detected. Exclusion of chlorides from the extraction is necessary, as the subsequent nitration seems sensitive to their presence. A lower salt concentration than that used gave erratic results and a high salt concentration precipitated solids into the bottom layer. Exclusion of water from the nitration mixture is imperative. The presence of oxidizable material, such as excessive amounts of alcohol from the extraction or stopcock lubricant, interfere probably by their effect in the nitration. Care in preventing this effect is fully as important as efficient extraction of the benzene in the carbon tetrachloride.

Acknowledgment

The writer wishes to express appreciation for the interest taken by A. Izsak in this work, and to the Commercial Solvents Corporation for permission to publish the results.

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Destruction of Organic Matter in Plant Material by the Use of Nitric and Perchloric Acids

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THE destruction of organic matter by some form of ashing generally precedes the determination of the mineral constituents in plant material. Two undesirable features of the ashing process suggest the need of a wet oxidation method similar to the Kjeldahl digestion: (1) The method of ashing commonly used for calcium and magnesium determinations is not applicable for potassium and phosphorus determinations on account of the loss of the more volatile compounds of potassium and phosphorus while ashing; and (2) the residues after ashing may be in a slowly soluble form.

Perchloric acid either alone or in mixtures with other acids has been widely used in the oxidation of organic materials of animal origin previous to the determination of the mineral constituents. Kahane and associates (*4*) have made the most comprehensive study of these methods and have developed a method for determining silica in plant materials (*5*). Winter and Bird (*11*) have used perchloric acid similarly for determining aluminum in plants.

The properties of perchloric acid, as well as those of the perchlorate ion, make it a very desirable oxidizing agent for the analysis of organic substances. No water-insoluble perchlorates of the metals have been reported. Furthermore, cold perchloric acid, either dilute or concentrated, is not affected by ordinary reducing agents. The dehydrating action of perchloric acid on silica, shown by Willard and Cake (*10*), aids in the quantitative separation of silica.

Since hot concentrated perchloric acid may react violently with organic substances, the reaction intensity must be controlled. It has been found advisable to pretreat samples of plant material with nitric acid before adding perchloric acid. With substances very high in fat it may be necessary to pretreat the sample several times with nitric acid before it can be oxidized with perchloric acid without a loss of a portion of the sample. The perchloric acid should be diluted with water and nitric acid.

Experimental Procedure

The following method of wet oxidation was applied to a wide variety of plant materials, including sweet clover (roots and tops), alfalfa hay, red clover hay, alsike clover hay, timothy hay, redtop hay, wheat straw, cornstalks, corncobs, corn (grain), and soy beans:

Place a 4-gram sample of the material to be oxidized in a 400-ml. beaker and add 10 ml. of nitric acid (sp. gr. 1.42). Cover the beaker with a watch glass and heat gently until any rapid initial reactions have subsided. Then heat to boiling and boil until the contents of the beaker are almost dry. Remove the beaker from the hot plate and add 10 ml. of dilute nitric acid (1 to 1) and 10 ml. of perchloric acid (70 to 72 per cent). Replace the cover glass and heat very gently to a low boiling temperature (avoid superheating). Maintain this temperature until all organic material has been removed from the sides of the beaker and from the solution, which will be indicated by a colorless or slightly colored solution. Remove the cover glass, allow the beaker to cool a few minutes, and wash any adhering salts into the beaker. (If the cover glass is washed with perchloric acid, the contents of the beaker need not be cooled.)

Evaporate to dryness at a temperature just below the boiling point in a clean hood. If potassium is to be determined on the residue, the ammonium salts should be removed at this point. After the removal of ammonium salts, add 5 ml. of hydrochloric acid (1 to 1) and 10 ml. of water. Heat until all salts are dissolved. Filter into a suitable volumetric flask. Wash the silica residue thoroughly with hot water and make the filtrate up to volume. Aliquot portions of the filtrate may be taken for subsequent analyses.

The above method was applied to the plant materials studied and calcium, magnesium, potassium, and phosphorus were determined. Known amounts of calcium from a standard solution of calcium acetate, magnesium from a standard solution of magnesium sulfate, and potassium and phosphorus from a standard solution of potassium dihydrogen phosphate were then added to a duplicate sample of the material and the determinations repeated, using the same procedure. The acids and salts used were taken from the usual laboratory stock of C. P. reagents. Calcium was precipitated as the oxalate and titrated with permanganate as directed by Wiley (*9*). Magnesium was determined by the method of Handy (*2*) as modified by Truog and Chucka (*8*). The method of Schueler and Thomas (*6*) was used for potassium. Phosphorus was precipitated as the phosphomolybdate and titrated with sodium hydroxide according to the method given by Treadwell and Hall (*7*). Table I shows the amounts of calcium, magnesium, potassium, and phosphorus recovered.

Table I. Recovery of Phosphorus, Potassium, Calcium, and Magnesium Added to Plant Material and Oxidized with Perchloric Acid

	Added, Mg.	Total, Mg.	Recovered, Mg.	Added, Mg.	Total, Mg.	Recovered, Mg.
	Phosphorus			Potassium		
Wheat straw	0	2.50	0	0	3.29	0
	2.00	4.50	2.00	0.60	3.91	0.62
	2.00	4.48	1.98	0.60	3.94	0.65
Sweet clover	0	2.00	0	0	1.92	0
	2.00	4.00	2.00	0.60	2.46	0.54
	2.00	3.95	1.95	0.60	2.49	0.57
	Calcium			Magnesium		
Wheat straw	0	8.2	0	0	3.01	0
	14.5	22.6	14.4	7.10	9.90	6.89
	14.5	22.6	14.4	7.10	9.99	6.98
Sweet clover	0	31.4	0	0	10.76	0
	14.5	45.9	14.4	7.10	17.91	7.15
	14.5	45.5	14.1	7.10	17.82	7.06

Table II. Total Calcium and Total Magnesium Found in Plant Material

(When oxidized with nitric-perchloric acid and when ashed without treatment according to A. O. A. C. method)

	Sample Number	Calcium By $HClO_4$	Calcium By ashing	Magnesium By $HClO_4$	Magnesium By ashing
		%	%	%	%
Wheat straw	902	0.38	0.30	0.14	0.11
	907	0.22	0.18	0.10	0.08
Sweet clover tops	W407	1.58	1.53	0.55	0.50
Sweet clover roots	N309	0.36	0.29	0.38	0.23
Sweet clover tops	C	0.74	0.76	0.61	0.67
Sweet clover roots	C	0.18	0.17	0.31	0.25
Redtop hay	WS	0.26	0.18	0.27	0.16
Timothy hay	R408E	0.30	0.19	0.17	0.16
Alfalfa hay	R409E	2.24	2.29	0.51	0.51

Table III. Total Phosphorus and Total Potassium Found in Plant Material

(When ashed with H_2SO_4 (method given by Wiley) and oxidized with nitric-perchloric acid)

	Sample Number	Phosphorus By $HClO_4$	Phosphorus By ashing	Potassium By $HClO_4$	Potassium By ashing
		%	%	%	%
Alfalfa hay	401	0.15	0.14	0.96	0.83
	403	0.20	0.22	0.73	0.69
	404	0.20	0.23	0.93	0.83
Red clover hay	408	0.20	0.20	0.80	0.67
	409	0.20	0.21	0.96	0.93
Alsike clover hay	401	0.15	0.15	1.16	0.99
	402	0.29	0.25	1.12	1.01
Wheat straw	902	0.25	0.22	1.69	1.50
	907	0.25	0.22	2.33	2.13

In order to test the accuracy of the nitric-perchloric acid method of destroying organic matter a corresponding set of samples was ashed, and calcium, magnesium, potassium, and phosphorus were determined as before. The method of the Association of Official Agricultural Chemists (*1*) was used for ashing the samples previous to the determination of calcium and magnesium, and the sulfuric acid method of Wiley (*9*) was used for potassium and phosphorus. As a further comparison, the method of Howk and DeTurk (*3*) was used for phosphorus. Samples of wheat straw, redtop hay, sweet clover tops, and sweet clover roots were found to contain 0.26, 0.15, 0.18, and 0.32 per cent of phosphorus, respectively, by the Howk and DeTurk method, as compared to 0.27, 0.16, 0.19, and 0.32 per cent by the nitric-perchloric acid method. The results of the other comparisons are given in Tables II and III.

Discussion of Results

The amounts of calcium, magnesium, potassium, and phosphorus added were very satisfactorily recovered with the use of the nitric-perchloric acid procedure (Table I).

Tables II and III show that there is not always good agreement between the nitric-perchloric acid and the ashing methods. It will be noted from Table II that in cases of disagreement calcium and magnesium are always lower when the samples are ashed. With the nitric-perchloric acid method one obtains a white residue of dehydrated silica, but when the sample is ashed for calcium and magnesium determinations, the residue is usually gray, indicating the incomplete oxidation of carbon. Furthermore, the calcium and magnesium in the ash are not readily soluble in the dilute acid used in extraction. Low results under such conditions suggest the incomplete removal of calcium and magnesium from the residue obtained upon ashing. Likewise, the ashing method for potassium tends to give lower results than the nitric-perchloric acid method. Since potassium compounds are volatile at high temperatures, a loss of potassium might be expected in using the ashing procedure.

The results of the three methods used for the phosphorus determinations agree very closely.

In view of these results and the plausible explanations thereof, it would seem that the proposed method of wet oxidation of this class of materials is from the standpoint of both accuracy and convenience superior to the ashing methods.

Summary

A method involving the wet oxidation of the organic matter in plant materials previous to the determinations of calcium, magnesium, potassium, and phosphorus has been devised. This method has been found to be rapid in that only one sample is required for the four determinations. The calcium, magnesium, potassium, and phosphorus are left in a condition in which they are readily soluble in dilute acids and no loss through volatilization of phosphorus or potassium was encountered.

The method used for preventing violent reactions between the perchloric acid and the organic substances was found to be effective in all cases.

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"Cold Light" Filter Developed

A filter for obtaining "cold light" has been developed by K. S. Gibson, chief, colorimetry section, National Bureau of Standards. This filter transmits a very narrow band in the green, and the luminous efficiency of this transmitted energy is extremely high—about 99 per cent of the maximum possible. The result is "cold light" or light practically without heat.

The transmitted band of light has a wave length of 560 millimicrons, a spectral region which is of particular importance in the colorimetry of sugar solutions, in optical pyrometry, in abridged spectrophotometry, and in photometry. Four components are used in the construction of the filter, two being made of Corning and two of Jena glass.

Solutions for Colorimetric Standards

VI. Ferric Chloride

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FOR the preparation of certain colorimetric standards various individuals (*1*) have proposed aqueous solutions of ferric chloride acidified with hydrochloric acid. Apparently recognizing some correlation between the hue of the solution and the amount of acid used, Arny made the acid concentration 1 per cent.

In preparing and using such a standard it is desirable both to recognize the factors affecting its color and to specify a set of conditions, following which will yield a reproducible system. The object of the present study, therefore, was to determine the significant facts concerning the colorimetric characteristics of the solution, including quantitative measurements, by means of a new spectrophotometer, of the effect of different amounts of acid.

A number of observations related to this problem have been previously reported as facts. The pale yellow hue of a freshly prepared, dilute aqueous solution becomes brownish on standing at room temperature, because of the formation of a sol of hydrous ferric oxide (*6*). This hydrolysis may be reversed by a small quantity of hydrochloric acid (*20*), but the resulting brilliance is not quite that of the original (*18*). The more dilute the unacidified solution, the less is the proportion of total iron present in true solution (*10, 19*). Acid stabilizes the solution (*15*). Adding concentrated hydrochloric acid turns a dilute, aqueous solution a deep, yellowish brown (*19*). This reaction, together with several of a similar nature between such a solution and various other reagents, indicates the formation of complex ions (*6, 15, 19, 21*). Over considerable ranges of concentration, Beer's law does not hold for solutions containing some acid (*11, 12*). The character and intensity of absorption of light by the solution depends upon the concentration, hydrolysis, and acidity (*8*).

Experimental Work

MATERIALS. Using ferric chloride, prepared by chlorinating iron wire (*2*), and concentrated hydrochloric acid, two stock solutions were prepared, one 4.10 *M* in ferric chloride and 0.1 *M* in acid, and one 10.9 *M* in acid only. Mixtures of these with water provided the different concentrations desired. Colloidal dispersions of hydrous ferric oxide were made by adding definite amounts of the stock solution of ferric chloride to boiling water and diluting to 100 ml. when cool.

PROCEDURE. The transmission measurements were made with a new photoelectric spectrophotometer built by the General Electric Company according to the design of A. C. Hardy. As the literature thus far contains only an abstract (*9*) concerning the principle of the instrument and a paragraph (*16*) on its construction, brief reference is made here to significant items regarding its use.

The assembly consists essentially of two units, a manually adjusted double monochromator and an automatic balancing photoelectric polarizing photometer. The photoelectric cell serves merely as a null device for detecting differences in intensity in the two light beams entering an integrating sphere. In operation a Rochon prism is rotated automatically until the two light beams match in intensity. At this point the percentage transmission may be read directly on a counter connected in the automatic mechanism.

The operation of this instrument was relatively simple, measurements being made by setting the wave-length scale, adjusting the three slits to give the desired width of spectral band at the given wave length, and reading the transmission on the photometer scale. The general practice was to make readings at intervals of 10 mμ from 400 to 700 mμ and then to check the readings back to the starting point. All data were obtained by dividing the transmission for the solution by that for the solvent. Measured cells were used and the data calculated to a thickness of 10.0 mm. by means of a special Keuffel and Esser slide rule based upon the application of Lambert's law.

To test the accuracy of the instrument the wave-length scale was calibrated in terms of lines from a mercury arc lamp and a helium tube (*7*), and the photometer scale was checked before each series of measurements by means of Bureau of Standards glasses (blue, amber, and red). Two solutions recommended by the Bureau of Standards (*5*) served to supplement the glasses. It is believed the calibration rendered the wave-length values accurate to 1 mμ. Since the instrument checked the values for the standard glasses within 0.5 per cent, the error in the transmittancies may be expected to be of this order of magnitude. The readings going up and down any curve were generally reproducible within ±0.2 per cent, indicating satisfactory precision. The average was taken for the values obtained going in the two directions. For relatively flat parts of a curve the slits were set for a 10 mμ band and then reduced for the steep parts to 5 or 3 mμ. These narrower bands somewhat decreased the sensitivity and precision.

It seems appropriate to mention certain advantages of the instrument in comparison with the visual one used for previous papers in this series. Of outstanding interest was the elimination of the personal equation in matching intensities, with its attendant optical fatigue. The time required for operation was much less. With the sample and light source nearly 3 meters apart and with most of the optical system between them, heating of the sample was practically eliminated and only monochromatic light passed through it. Illumination of the dark room did not affect the measurements. The accuracy and precision in the blue and red regions was undoubtedly much superior to that obtained in the previous

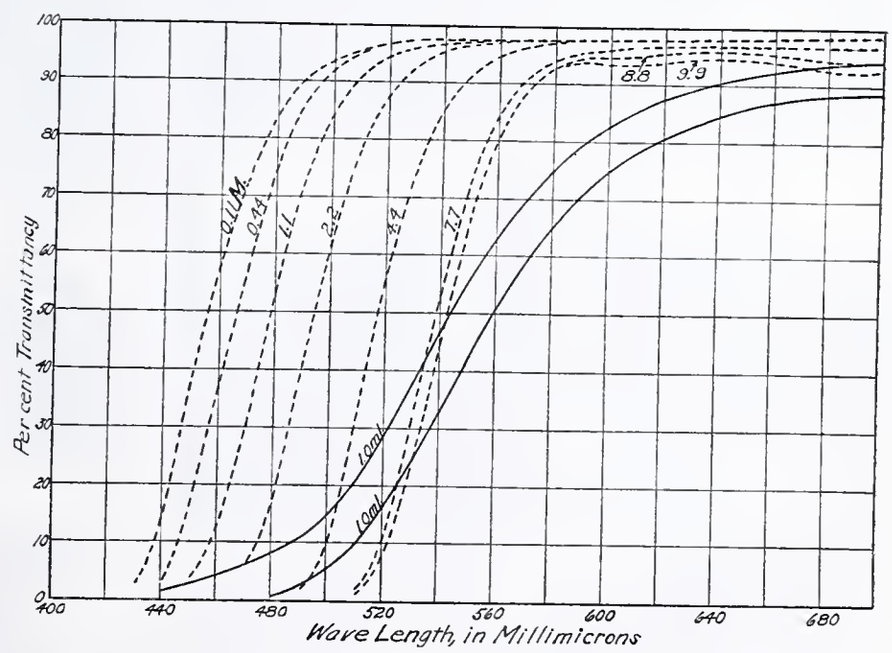

FIGURE 1. SPECTRAL TRANSMISSION CURVES

Broken lines, solutions 0.1 *M* in ferric chloride and varying molarities in hydrochloric acid. Solid lines, colloidal dispersions prepared from 1 and 10 ml. of a solution 4.1 *M* in ferric chloride and 0.1 *M* in hydrochloric acid.

papers. Preliminary checking of a few solutions has indicated considerable uncertainty in values there reported for wave lengths below 450 and above 650 mμ. At that time, however, the data were the best that could be obtained with the facilities available.

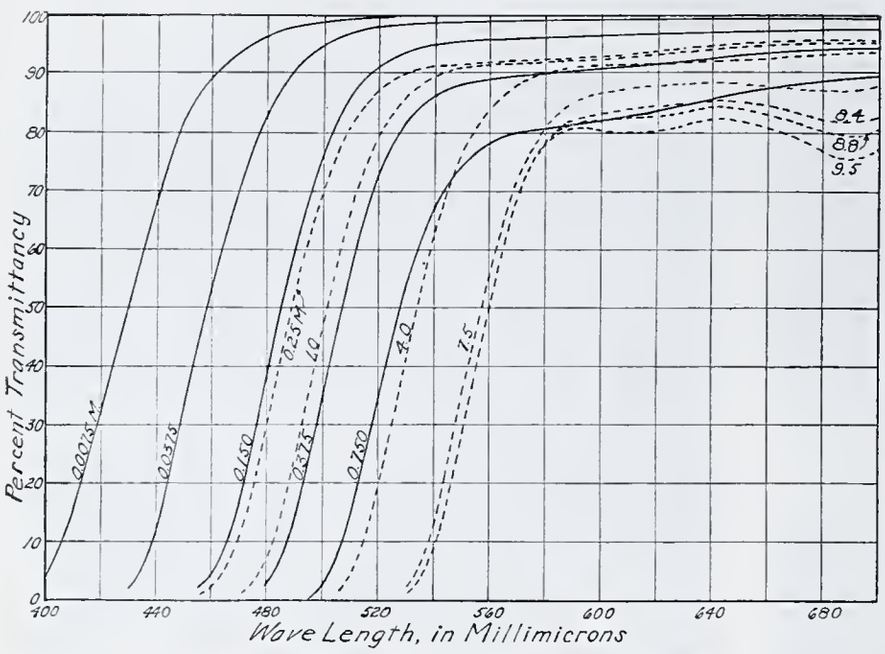

FIGURE 2. SPECTRAL TRANSMISSION CURVES

Broken lines, solutions 0.3 *M* in ferric chloride and varying molarities in hydrochloric acid. Solid lines, solutions 1.0 *M* in hydrochloric acid and varying molarities in ferric chloride.

In addition to the determination of the transmission data qualitative experiments were made which resulted, in general, in a confirmation of the observations recorded in the literature cited.

Figures 1 and 2 with wave lengths as abscissas and transmittancies as ordinates, represent typical data. The solutions studied ranged in concentration from 0.0155 to 1.000 *M* in ferric chloride, and from 0.0275 to 10.66 *M* in hydrochloric acid.

Discussion

The curves shown in Figures 1 and 2 are indicative of the absorptive characteristics of the solutions. Only at the higher acidities is there evidence of divergence from the general regularity. On one solution, 0.1 *M* in ferric chloride and 1.1 *M* in acid, readings were made each 2 mμ with a 5 mμ band, but there were revealed at this slit width no maxima nor minima, such as those recently reported by Brode (*3*) for cobaltous chloride or by Zscheile (*22*) for chlorophyll. These data, together with visual observation of the systems, indicate that the solutions most likely to be of use for colorimetric standards are those showing smooth curves with acidities under 5 *M*.

Several individuals have reported (*11, 12*) that the brownish hue in very acidic solutions reaches a maximum when the concentration of acid is approximately 9 *M*, the exact point depending upon the concentration of iron. For this phenomenon Figure 1 does not show the expected reversal of curves. Solutions of such acidities are probably of no value for colorimetric work.

In Figure 1 the curves for the interesting colloidal dispersion of hydrous ferric oxide should be considered as merely illustrative of the form characteristic of such systems. While a carefully prepared dispersion seems relatively stable, its reproducibility is very questionable unless under very closely controlled conditions. Apparently it is a problem of obtaining particles of the same size.

Calculation of monochromatic data (*13*) for solutions 0.5 *M* in ferric chloride and 0.275 to 8.8 *M* in acid showed that the colorimetric purity is high in all cases (97 to 99 per cent). The relative brilliance decreases with increasing acidity at least up to 8.8 *M* while the dominant wave length shows the reverse change.

Solutions 0.3 *M* in ferric chloride and 0.25, 1.0, and 7.5 *M* in acid were diluted to five times their original volume, keeping the acidity constant, and measured in 5-cm. cells. The curve for the data thus obtained for the 0.25 and 1.0 *M* solutions came 6 to 10 mμ to the left of those in Figure 2 for the same solution measured before dilution in 1-cm. cells. For these two concentrations this represents distinct divergence from conformity to Beer's law, but the data obtained in the same way for the 7.5 *M* solution were practically identical.

Little or no dichromatism was indicated for a solution 0.25 *M* in ferric chloride and 0.44 *M* in acid when the luminosities were calculated according to Clark's method (*4*) and plotted against wave lengths.

The curves for three solutions, 0.1666 *M* in ferric chloride and 0.27 *M* in acid, one 5 years old, one 18 months old, and one freshly prepared, each made by a different individual, checked each other within the experimental error, confirming Arny's observations (*1*) on stability and reproducibility. However, solutions 0.02 *M* in acid were no t sufficiently acidic to prevent hydrolysis, with resultant fading and formation of a precipitate.

Sidgwick has discussed (*17*) certain striking properties of ferric chloride which he attributes to its electronic structure. In a variety of organic solvents carbon tetrachloride alone failed to dissolve it in substantial amounts. Curves for solutions in chloroform and in glacial acetic acid resembled closely those shown here for the lower acidities. Many of the organic solutions fade more or less rapidly (*14*), presumably from the reduction of the iron, rendering them worthless as colorimetric standards.

Summary

Attention has been directed to various factors affecting the color of solutions of ferric chloride. Spectral transmission curves show the type of absorption under different conditions. The best range of concentrations for colorimetric standards is probably from 0.5 to 0.02 *M* in ferric chloride and from 5.0 to 0.05 *M* in hydrochloric acid.

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Combination of Catalysts to Reduce Digestion Time in Determination of Nitrogen

I. In Organic Compounds

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CONFIRMING the work of other investigators, it has been found in this laboratory (*3*) that 30 per cent hydrogen peroxide hastens the digestion in the determination of nitrogen in organic compounds by the Gunning process. Various combinations of catalysts, with and without strong hydrogen peroxide, have also been used in this laboratory in the determination of nitrogen in dairy products (*6*). In this communication, there is reported the quantitative reduction in time when nitrogen is determined in organic compounds with the aid of strong hydrogen peroxide and a mixture of copper, mercury, and selenium as catalysts.

In every case, the samples containing catalysts cleared much more rapidly than the controls. The use of the combination of copper, selenium, and mercury effects the greatest saving of time. In some cases the use of strong hydrogen peroxide with these three catalysts somewhat reduces the digestion time over that obtained when these catalysts were used without the hydrogen peroxide, but not enough time was saved to warrant the additional expense and trouble. The use of selenium alone or in combination with other catalysts has been claimed by several investigators (*2, 4, 5, 7*) to cause some loss of nitrogen. The results of the present experiments, however, show no loss of nitrogen by the use of this catalyst. Use of a mixture of selenium, copper, and mercury for the determination of nitrogen in organic compounds does not seem to have been tried by other investigators.

Table I. Determination of Nitrogen in Organic Compounds

Compound	Theoretical	Gunning Method		1 g. $CuSO_4$	0.5 g. HgO	$CuSO_4$ + HgO + Se		$CuSO_4$ + HgO + Se + H_2O_2	
	%	Min.	%	Min.	Min.	Min.	%	Min.	%
Acetanilide	10.37	90	10.26	21	20	10	10.41	10	10.33
Acetphenetidin	7.70	119	7.70	16	16	9	7.68	10	7.66
o-Aminobenzoic acid	10.21	60	10.15	28	31	18	10.16	18	10.10
m-Aminobenzoic acid	10.21	61	10.18	29	42	13	10.16	12	10.17
p-Aminobenzoic acid	10.21	60	10.20	25	33	13	10.13	15	10.11
dl-d-Amino-*n*-butyric acid	13.58	128	13.57	38	42	22	13.69	16	13.61
Aminocaproic acid	10.68	254	10.74	26	27	21	10.63	18	10.67
Aminocaprylic acid	8.79	250	8.63	28	32	22	8.84	18	8.73
Amino-isobutyric acid	13.58	131	13.59	36	41	21	13.48	16	13.45
Benzidine	15.21	300	15.36	26	25	9	15.16	8	15.20
p-Bromoacetanilide	6.54	140	6.45	29	33	21	6.42	17	6.58
3-Bromo-4-acetylamino toluene	6.14	210	5.94	29	33	21	6.12	17	6.22
p-Bromoaniline	8.14	120	8.05	22	29	18	8.09	18	8.20
o-Chloroacetanilide	8.26	212	8.26	30	34	11	8.17	12	8.24
p-Chloroaniline	10.99	230	10.85	29	34	18	10.88	18	10.85
1,4-Diaminobutane-hydrochloride	17.39	165	17.38	27	25	17	17.45	17	17.32
p-Dimethylaminobenzaldehyde	9.39	214	9.26	33	39	22	9.26	22	9.24
o-Tolylurea	18.65	210	18.44	29	27	19	18.62	17	18.79
p-Tolylurea	18.65	215	18.48	30	27	20	18.59	17	18.77
2,4,6-Tribromoaniline	4.25	60	4.30	28	31	23	4.30	17	4.28

The method employed was the Gunning modification of the original Kjeldahl method, which is official with the Association of Official Agricultural Chemists (*1*).

In each of a number of digestion flasks, 0.25 gram of the organic compound was placed with 10 grams of nitrogen-free potassium sulfate and 20 cc. of concentrated sulfuric acid. To four of the flasks were added the following catalysts: (1) HgO, 0.5 gram; (2) $CuSO_4.5H_2O$, 1 gram; (3) HgO, 0.3 gram; $CuSO_4.5H_2O$, 0.5 gram; and Se, 0.1 gram; (4) the same ingredients as (3) with the addition of 1 cc. of strong hydrogen peroxide every 5 minutes until the solution cleared. The fifth flask contained no added catalyst. The contents of each flask were digested over electrically heated plates, all units of which were of the same construction and gave the same amount of heat. Each sample was heated until the liquid cleared.

Table I gives the comparisons of the times necessary for the clearing to take place and some quantitative results.

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A Color Test for the Identification of Mono-, Di-, and Trinitro Compounds

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IN SPITE of the fact that most color reactions are viewed with suspicion in qualitative organic analysis, there are certain instances where they may conserve time and lead to many short cuts in the identification of a given compound. In other cases color tests serve to detect traces of impurities in a compound, the presence of which it might otherwise be difficult to show. In view of these facts the work reported herein was undertaken.

Janovsky and Erb (*3*) showed that violet or reddish brown colors were obtained when nitroazo compounds were treated with acetone and potassium hydroxide. In 1891 Janovsky (*2*) studied the reaction between acetone and the dinitro substitution products of benzene, toluene, and napthalene in the presence of potassium hydroxide. A year later von Bitto (*1*) reported the action of aldehydes and ketones on *m*-dinitrobenzene, dinitrotoluene, and α-dinitronaphthalene with potassium hydroxide, as well as of certain trinitro compounds. The mechanism of the reaction between acetone and 2,4-dinitrochlorobenzene in the presence of sodium hydroxide has been explained by Reitzenstein and Stamm (*4*).

Taylor and Rinkenbach (*6*) and Rudolph (*5*) have reported the colors produced by a few mono-, di-, and trinitro bodies under the aforementioned conditions. Taylor and Rinkenbach point out that the color produced by trinitro compounds will obscure those produced by dinitro bodies when the two types are present in mixtures. The authors have confirmed this observation.

It seemed desirable to extend the work of previous investigators in this field and to determine, if possible, the limitations of the color test in detecting nitro compounds. In this paper are given data on many mono-, di-, and trinitro compounds of benzene, showing the effect of the presence of various substituted groups, such as aldehyde, alkyl, amino, ester, carboxyl, halogen, hydroxyl, and methoxy, as well as the position of the nitro groups in the molecule, on the color produced.

Phenomenal as it may seem, mononitro compounds give no color with the reagent, dinitro compounds give a purplish blue color, while trinitro compounds produce a blood red color, except where an amino, substituted amino, or hydroxyl group is present. Acylation of the amino or hydroxyl group does not alter the inhibiting effect of such groups on the color test. The substitution of an alkyl group for an amino hydrogen does not alter the inhibition of the amino group, whereas the substitution of a methyl group for enolic-hydrogen permits the compound to respond to the general color test. Noteworthy examples are 2,4-dinitroaniline, 2,4-dinitrophenol, 2,4-dinitroacetanilide, 2,4-dinitrophenylacetate, 2,4-dinitrodiethylaniline, and 2,4-dinitroanisole.

In cases where the benzene nucleus is richly substituted, as in 2,4-dinitromesitylene, 2,4,6-trinitromesitylene and 2,-

TABLE I. COLOR IN MONONITRO COMPOUNDS

Compound	Reagent	Diluted with H_2O	HCl Added	CH_3COOH Added	Acid Solution Treated with NaOH
p-Nitrochlorobenzene	None	None	None	None	None
p-Nitrobromobenzene	None	None	None	None	None
m-Nitroaniline	None	None	None	None	None
Nitrobenzene	None	None	None	None	None
m-Nitrobenzaldehyde	None	None	None	None	None
m-Nitrobenzoic acid	None	None	None	None	None
p-Nitrobenzoyl chloride	None	None	None	None	None
3-Nitro phthalic acid	None	None	None	None	None
p-Nitroanisole	None	None	None	None	None
o-Nitrotoluene	None	None	None	None	None
m-Nitrotoluene	None	None	None	None	None
p-Nitrotoluene	None	None	None	None	None
3-Nitro-4-aminotoluene	Orange	Yellow	No change	No change	No change
3-Nitro-4-aminotoluene benzoate	Reddish orange	Light yellow	Yellowish green	Yellowish green	Reddish orange

TABLE II. COLOR IN DINITRO COMPOUNDS

Compound	Reagent	Diluted with H_2O	HCl Added	CH_3COOH Added	Acid Solution Made Basic with NaOH On HCl soln.	On CH_3COOH soln.
m-Dinitrobenzene	Purplish blue	Light purple	Yellowish brown	Reddish purple	Red	Red
2,4-Dinitrochlorobenzene	Purplish blue	Light purple	Lemon yellow	Wine red	Wine red	Wine red
3,5-Dinitrobenzoic acid	Purplish blue	Light purple	Wine then pink	Dark blue	Purle	Purple
3,5-Dinitromethylbenzoate	Blue	Faint blue	Crimson then pink	Blue	Purplish blue	Blue
2,4-Dinitroanisole	Purplish blue	Faint violet	Greenish yellow	Purplish red	Wine red	Wine red
2,4-Dinitrothioanisole	Blue	Faint blue	Yellow	No change	Color restored	Color restored
2,4-Dinitrotoluene	Blue	Faint blue	Greenish yellow	Purple	Purplish blue	Purplish blue
2,6-Dinitro-*p*-cymene	Purplish blue	Faint violet	Light yellow	Faint reddish brown	Light yellowish brown	Faint pink
2,4-Dinitromesitylene	None	None	None	None	None	None
3,5-Dinitro salicylic acid	Yellow	Faint lemon yellow	Reddish orange	Pink	Yellow	Yellow
2,4-Dinitrophenylacetate	Reddish orange	Greenish yellow	None	Lemon yellow	Reddish orange	Yellowish orange
2,4-Dinitrophenol	Yellowish orange	Faint greenish yellow	Faint lemon yellow	Yellowish green	Yellowish orange	Yellowish orange
2,4-Dinitroresorcinol	Brownish green	Faint brownish green	Light brown	Greenish brown	Greenish brown	Greenish brown
2,4-Dinitroaniline	Red	Pink	Lemon yellow	Orange red	Red	Red
2,4-Dinitroacetanilide	Reddish orange	Greenish yellow	Color discharged	Color discharged	Original color restored	Original color restored
2,4-Dinitrodiethylaniline	Reddish orange	Pink green fluorescence	Color discharged	Color discharged	Reddish orange	Light reddish orange
p-Dinitrobenzene	Greenish yellow	Faint greenish yellow	Colorless	Colorless	Original color restored	Original color restored
o-Dinitrobenzene	None	None	None	None	None	None

TABLE III. COLOR IN TRINITRO COMPOUNDS

Compound	Reagent	Diluted	HCl Added	CH_3COOH Added	Acid Solution Made Basic with NaOH On HCl soln.	On CH_3COOH soln.
1,3,5-Trinitrobenzene	Red	Light red	Blood red	Wine red	Reddish brown	Blood red
2,4,6-Trinitrotoluene	Red	Faint pink	Red	Red	Red	Red
2,4,6-Trinitroanisole	Red	Faint pink	Orange red	No change	Orange yellow	Red
2,4,6-Trintrobenzoic acid	Red	Pink	Red	Red	Pink	Pink
2,4,6-Trinitrobenzaldehyde	Brownish red	Faint brownish red	Brownish red	Brownish red	Brownish red	Brownish red
2,4,6-Trinitrophenylhydrazine	Brownish red	Faint brownish red	Brownish red	Brownish red	Dark brownish red	Dark brownish red
2,4,6-Trinitrophenol	Reddish orange	Light orange red	Orange	Reddish orange	Yellowish orange	Reddish orange
2,4,6-Trinitrophenylacetate	Reddish orange	Greenish yellow	No change	Reddish brown	No change	Reddish brown
2,4,6-Trinitro-*m*-cresyl acetate	Orange yellow	Yellowish green	No change	Slightly darker	No change	Color lightened
2,4,6-Trinitro-*m*-cresol	Orange	Light lemon yellow	Lemon yellow	Lemon yellow	Reddish orange	Reddish orange
2,4,6-Trinitroresorcinol	Greenish yellow	Light greenish yellow	Orange yellow	No change	Greenish yellow	No change
2,4,6-Trinitroresorcinyl acetate	Greenish yellow	Light greenish yellow	No change	No change	No change	No change
2,4,6-Trinitromesitylene	None	None	None	None	None	None
2,4,6-Trinitro-1,3-dimethyl-5-ter-butyl benzene	None	None	None	None	None	None

4,6-trinitro-1,3-dimethyl-5-ter-butyl benzene, no color is produced.

The steric effect of the nitro group in the isomeric dinitrobenzenes is noteworthy. *m*-Dinitrobenzene readily responds to the test, *p*-dinitrobenzene gives a reddish yellow which soon passes into a greenish yellow color, while *o*-dinitrobenzene gives no color at all.

The test is extremely delicate in most cases—for example, 2,4-dinitrobenzene is sensitive to one part in 1,500,000. Since mononitro compounds fail to respond to the test, it is possible to detect traces of di- or trinitro compounds in mononitro compounds as impurities by this method, but it is not possible to detect dinitro compounds in the presence of trinitro compounds.

Procedure

One-tenth gram of nitro compound is dissolved in 10 ml. of acetone and 3 ml. of 5 per cent sodium hydroxide are added with shaking. At this point a purplish blue color will appear for dinitro compounds, while a blood red color is produced by trinitro bodies. Mononitro compounds fail to give a color. Exceptions to these tests have been discussed above. These colors are true only for the benzene series. If it is desired to produce a less intense color, a smaller amount of alkali should be used in the test.

In Tables I, II, and III are given the results with various nitro compounds under different conditions.

Summary

Mononitro compounds of the benzene series produce no color with the reagent, dinitro compounds a purplish blue color, and trinitro compounds a blood red color.

The presence of the amino, substituted amino, or hydroxyl group in the nucleus interferes with the test. Acylation of these groups does not remove the interference.

The test is extremely sensitive.

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An Improved Slow-Combustion Pipet for Gas Analysis

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SINCE 1876 when Coquillon (*3*) proposed the use of a platinum spiral for slow-combustion analysis of hydrocarbon gases, this method has come to be practically standard. In the usual method the combustion pipet is filled with oxygen or air and the combustible gas is slowly introduced at the top of the pipet where it comes in contact with the heated platinum spiral and combustion ensues (*2*, *4*). Improvements upon the basic design of this pipet have been made by Weaver and Ledig (*8*) and Matuszak (*7*).

A deposit of carbon is often found on the pipet wall above the spiral after a series of combustions, and when burning some gases such as isobutane, combustion is incomplete to the extent that when the gases are passed the second time over the hot spiral an explosion often occurs.

In one pipet designed to secure more perfect combustion and decrease the danger from explosions, the gas to be burned is introduced through a capillary platinum jet located in the side wall of the pipet and impinges directly upon the heated spiral (*1*). Convection in this case should aid in keeping the spiral surrounded by oxygen rather than hot products of combustion, yet it is possible that the combustible gas might be swept away before reaching the heated zone.

To secure safety in operation and accuracy in results, complete combustion must be secured, and the most logical method of securing complete combustion is to burn a preheated mixture of the combustible gas and an excess of oxygen. Any such mixture with a sufficiently high concentration of combustible to be useful in gas analysis is explosive, so the usual pipet cannot be used.

Drehschmidt (*5*) passed combustible mixtures through 100 mm. of platinum capillary tubing of 0.7 mm. internal and 2.5 mm. external diameter, which he heated by a Bunsen flame. His platinum tube deteriorated rapidly with use and had to be renewed because of leakage. Weaver and Ledig

(*8*) describe forms of glass or quartz capillary tubes containing fine heated spirals which are useful for determining small amounts of oxygen in a gas, or small traces of combustible in oxygen or air. Lutz (*6*) has found such apparatus not satisfactory for use in general slow-combustion analysis.

Design

In a preliminary design of a slow-combustion pipet in which the combustible gas could be mixed with oxygen and passed over an ignitor, the gas was led through 2.5 cm. of platinum tubing of 0.9 mm. internal and 1.0 mm. external diameter with an insert of 0.45-mm. platinum wire. The small annular space remaining for passage of gas prevented passage of flame or explosion wave for all combustible mixtures tried, including electrolytic gas at very low flow rates. One to two millimeters from the

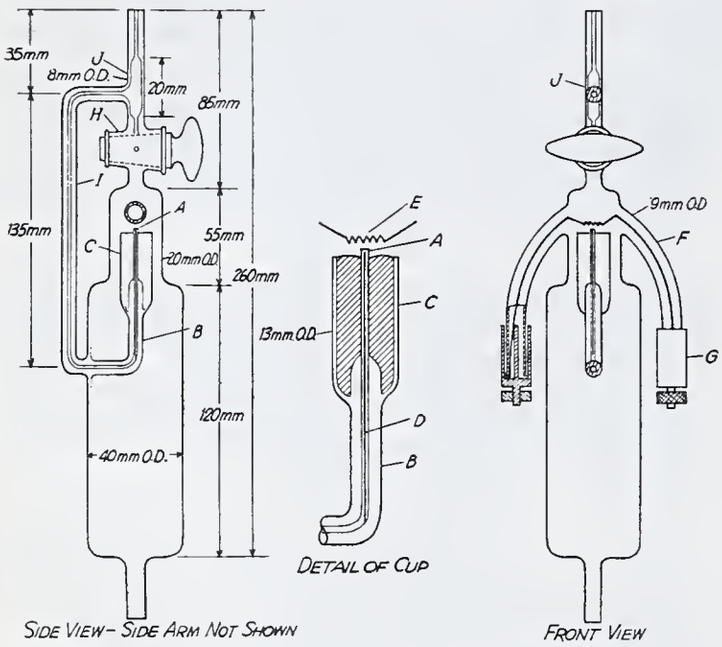

FIGURE 1. DIAGRAM OF PIPET

end of this inlet tube were placed the various ignitors. An unsupported platinum spiral, platinum spirals on quartz and refractory supports, and a refractory mixture containing thorium and aluminum oxides, alundum cement, and water-glass binder with internal spiral of platinum wire were tried as ignitors. It was found that, because of the radiating power of the refractories and the protection which they afforded the platinum wire, the gas could be burned more rapidly on them than on the bare platinum. However, this design was not satisfactory, as the tip of the platinum tube became hot enough to cause carbon deposition, even in the presence of 100 per cent excess oxygen. In a short time the tube became fouled, and the analyses were inaccurate. Unless the gas was passed into the pipet at a slow rate the platinum tube became overheated at a point dangerously near the inlet end. Consequently, some method of cooling the capillary was thought necessary, and the pipet illustrated was developed.

The pipet is constructed of Pyrex glass as shown in Figure 1. A platinum tube, *A*, 2.5 cm. long, 0.9 cm. internal diameter, is sealed into capillary *B* and projects 2 mm. above the level rim of cup *C*. A length of 0.45-mm. platinum wire, *D*, is inserted into the top of the platinum tube to the bend in *B*. A ten-turn helix, *E*, of 0.2-mm. platinum wire is supported 3 mm. above the tip of the tube by 0.45-mm. platinum leads which are brought into two side arms, *F*, to which steel terminals, *G*, are secured with sealing wax.

Operation

When the pipet is filled with mercury, the side arms and cup should be clean and dry. With stopcock *H* open, the mercury level is raised above the tip of the platinum tube. Stopcock *H* is then closed and mercury run into *B* until it rises in *I* above the level of *H*. By lowering the mercury level in *I* any air trapped in *B* is forced out by the rising mercury, and then with *H* open the remaining space in the pipet may be filled with mercury.

A sample of gas requiring from 40 to 60 cc. of oxygen for combustion is measured and stored in the potassium hydroxide pipet. After a thorough rinsing of the manifold and manometer with nitrogen, 100 cc. of oxygen are measured in the buret. With stopcock *H* open, oxygen is run into the pipet until the mercury level is 1 to 2 cm. below the rim of the cup. By closing *H* and raising the mercury level in the pipet, any mercury remaining in *I* or *B* is blown up into the enlarged section, *J*, above the stopcock. The mercury level is brought to just below the rim of *C* and the spiral heated to a bright red. With the combustion pipet shut off from the manifold, the remaining oxygen is thoroughly mixed with the combustible sample by passing back and forth from the potassium hydroxide pipet to the buret several times. With the pressures in the pipet and buret equalized and *H* always closed, the gas is allowed to flow slowly into the pipet. By decreasing the current through the spiral as the gas rate is increased, the sample may be burned as fast as 40 cc. per minute.

After all the gas has been passed into the pipet, 10 cc. are withdrawn and passed in again several times to burn the unexposed portions in the connection between buret and capillary tip, and then the entire volume is passed over the spiral a few times before determining the resulting volume and carbon dioxide. Any combustible gas in the potassium hydroxide or connections will yield an additional fraction of a cubic centimeter of contraction and carbon dioxide on a repeated series of passes over the spiral.

Performance

Typical combustion data on commercial hydrocarbon gases of unknown purity or composition were secured by the same operator to compare the performance of this new pipet with that of the standard Burrell pipet. Each column of Table I represents the average of three combustions.

On the basis of the values of n for saturated hydrocarbons (C_nH_{2n+2}), the percentage of ethane in the mixture is calculated to be 59.9 and 56.8 per cent by the new and Burrell pipets, respectively, compared with the measured value of 58.3 per cent.

TABLE I. TYPICAL COMBUSTION DATA

	Methane		Ethane		Methane, 41.74% Ethane, 58.26%	
	Burrell	New	Burrell	New	Burrell	New
Sample taken, cc.	23.65	22.70	16.98	18.82	19.75	20.38
Hydrocarbon in sample, cc.	23.33	22.38	17.36	19.32	19.31	20.10
Carbon atoms, calculated	1.215	1.189	1.914	1.865	1.612	1.594
Hydrocarbon found, per cent	98.65	98.60	102.29	102.65	97.77	98.62

It appears that the accuracy of results obtainable with this pipet is equal to the accuracy obtainable with the Burrell pipet. For the greatest accuracy, the platinum spiral should be located not less than 3 mm. above the tip of the platinum tube and the temperature of the platinum tube should be kept as low as possible.

This pipet offers the added advantage of complete safety in operation, as evidenced by the fact that over 125 combustions have been performed by both experienced and inexperienced analysts on a pipet of this type, using gases varying from methane-hydrogen mixtures to isobutane and *n*-pentane, with no flash-backs or explosions.

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Copper Determination by Alpha-Benzoin Oxime in Copper-Molybdenum Alloy Steels

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THERE are two methods in common use for separating the copper from copper-molybdenum alloy steels or from molybdenum alloy steels containing copper as an impurity.

In the first method the steel is dissolved in dilute sulfuric acid and, if vanadium is present, oxidized with potassium chlorate. Both copper and molybdenum are precipitated by hydrogen sulfide gas or sodium thiosulfate. The precipitate is filtered and ignited to oxide. The oxides are fused with potassium bisulfate and the melt is dissolved with dilute hydrochloric acid. The copper is precipitated from the slightly acid (hydrochloric) solution by 5 per cent sodium hydroxide. The paper holding the copper hydroxide is fumed with sulfuric and nitric acids and the solution filtered. The filtrate is again saturated with hydrogen sulfide gas, filtered, and the residue ignited to oxide. This method is long and the work is very delicate in regard to finding a suitable condition to precipitate the copper with the exact amount of sodium hydroxide. Also, ignition of copper sulfide to oxide is not an easy task.

The second method is similar to the first one in regard to dissolving and precipitating the copper and molybdenum either by hydrogen-sulfide gas or sodium thiosulfate. The sulfides of both metals are ignited and the oxides are dissolved in dilute nitric acid. The solution is filtered and copper is separated by electrolysis. This method is also long, and complete deposition of copper by electrolysis is not sure, especially when the copper content of the steel is low.

The obstacles mentioned above are removed and the time is considerably shortened by using α-benzoin oxime for precipitating the copper.

Procedure

Transfer 2 to 5 grams of the sample, depending on the copper content of the steel, to a 600-cc. beaker. Add 50 to 100 cc. of 10 per cent sulfuric acid and heat until action is complete.

If vanadium is absent, dilute the solution to 250 cc. with hot distilled water and heat to boiling. Add 1 gram of sodium thiosulfate for each gram of steel, dissolved in 10 to 50 cc. of water. Boil the solution 10 to 15 minutes and allow precipitate to settle. If vanadium is present, add a few crystals of potassium chlorate to the sulfuric acid solution, and heat to dissolve the insoluble. Dilute to 400 cc. with hot water. Saturate with hydrogen sulfide gas for 15 minutes, and allow precipitate to settle.

Filter on a close paper, using slow suction, and wash the paper and the beaker a few times with hot 1 per cent sulfuric acid. Transfer the paper to a silica crucible and ignite at dull red heat. Cool the crucible, add 10 cc. of hydrochloric acid, and heat to dissolve the residue. Transfer the solution to a 400-cc. beaker, add 2 to 3 drops of nitric acid, and treat with excess of ammonia. Heat to boiling and filter into a 600-cc. beaker. Wash with hot ammoniacal water and discard the paper.

Dilute the filtrate to 250 cc. with water and heat to boiling. Add 10 to 15 cc. of a 2 per cent alcoholic solution of α-benzoin oxime slowly and while stirring constantly. Boil for 1 minute. Add some ashless pulp and filter on a rapid paper. Wash 5 or 6 times with hot 3 per cent ammonia water, and ignite the paper in a silica crucible. Cool and weigh the precipitate. Multiply the weight by 80 and divide by the number of grams of the sample, to get the copper content of the steel.

Reactions involved in the procedure:

$$CuSO_4 + H_2S = CuS + H_2SO_4$$
$$CuO + 2HCl = CuCl_2 + H_2O$$
$$CuCl_2 + 4NH_4OH = Cu(OH)_2{\cdot}2NH_4OH{\cdot}2NH_4Cl$$
$$Cu(OH)_2{\cdot}2NH_4OH{\cdot}2NH_4Cl + (C_6H_5)_2{\cdot}CH(OH){\cdot}C{:}(NOH) = Cu(C_6H_5)_2{\cdot}CHO{\cdot}C{:}NO + 2H_2O + 2NH_4OH + 2NH_4Cl$$
$$Cu(C_6H_5)_2{\cdot}CHO{\cdot}C{:}NO + \text{heat} = CuO$$

If steel is alloyed with tungsten, transfer 2 to 5 grams of the sample to a 600-cc. beaker, add 50 cc. of concentrated hydrochloric acid, and heat until action is complete. Add 5 cc. of nitric acid and evaporate to dryness. Cool. Add 25 cc. of hydrochloric acid and heat to dissolve the iron, chromium, etc. Add a few crystals of potassium chlorate, and continue heating until tungstic oxide is completely separated. Add 150 cc. of water, heat to boiling, and allow precipitate to settle. Filter and wash with cold 5 per cent hydrochloric acid about 10 times. Add 10 to 25 grams of citric acid and render the solution alkaline by ammonia. Acidify the solution with hydrochloric acid and add 2 cc. excess for each 100 cc. of solution.

Heat to boiling and saturate with hydrogen sulfide gas. Filter and proceed in the same way as described above.

Experiments proved that the most suitable medium for the precipitation of copper by α-benzoin oxime was ammoniacal solution. Molybdenum, which can be quantitatively precipitated in acid solution, yields no precipitate in ammoniacal solution.

This method functions on all grades of steel where molybdenum and copper are present, either as impurities or as alloying elements. The accuracy has been checked against a complete range of U. S. Bureau of Standards steel samples (Table I). By means of the method described above accurate copper analysis can be made in 1 hour, whereas the former methods required from 3 to 6 hours.

TABLE I. CHECK ANALYSES

Standard Samples	Average Cu Reported	Results by Method
	%	%
20c	0.255	0.263
30c	0.099	0.105
32b	0.117	0.13
33b	0.114	0.120
35a	0.267	0.27
72	0.064	0.07
73	0.033	0.04
101	0.055	0.062
106	0.142	0.16
111	0.122	0.135

Feigl (*1*) has reported on the use of α-benzoin oxime for copper determination in other materials.

Literature Cited

(1) Feigl, F., *Ber.*, 56, 2083 (1923).

RECEIVED February 1, 1935.

NEW LINES DISCOVERED IN COPPER SPECTRUM. Thirty new lines in the arc spectrum of copper have been discovered by C. C. Kiess of the National Bureau of Standards, using infra-red sensitive photographic plates. All of these lines, except one, are accounted for as combinations between terms derived from an analysis of the previously known spectrum.

One of the major duties of the bureau's spectroscopy laboratory, it is pointed out, is to furnish as complete descriptions of the spectra of the chemical elements as modern observational methods will permit. These serve as reference standards for other workers in this field. For the element copper, radiometric observations made elsewhere several years ago failed to reveal any lines in its arc spectrum in the range from 8100 to 12,000 Å. The new types of photographic plates that are sensitive to infra-red light now show this region to contain many lines of great importance in working out the atomic structure, it was stated.

Electrometric Titration

Device for Automatically Stopping at a Predetermined End Point

W. E. SHENK and F. FENWICK, Research Laboratory, United States Steel Corporation, Kearny, N. J.

A device is described which automatically stops an electrometric titration by utilizing the sudden change developed in the potential difference between two dissimilar metal electrodes at the end point to actuate a shut-off. The instrument is made of easily obtainable parts and requires no source of power besides the lighting circuit and a single dry cell; it is practically independent of fluctuations in line voltage. Its usefulness is demonstrated by application to three titrations—the titration of Fe^{++} with potassium dichromate, of $Cr_2O_7^{--}$ with Fe^{++}, and of Zn^{++} with potassium ferrocyanide.

THIS device makes use of the potential difference between the two electrodes involved in an electrometric titration as a means of stopping the addition of the titrating agent at a set end point. It is positive in action, is made up largely of standard parts, and in operation requires little trained attention; the reproducibility of its end point equals, or closely approaches, that obtained with careful manual operation requiring continuous attention during the whole course of the titration. The only analogous automatic device of which the authors are aware is that described by Müller and Partridge (*1*), who used the color-change of an indicator as a means of actuating a photoelectric cell to shut off the flow of the titrating agent.

If the potential between the two electrodes is to be used to actuate the control, the circuit must be such that the current drawn from the titration cell is exceedingly small; otherwise there will be serious polarization of the electrodes which is likely to alter the electromotive force of the cell so much as to make uncertain the determination of the true end point. Moreover, there is the condition, applicable to any accurate electrometric titration, that the development of the electrode potential must very nearly keep pace with the addition of the titrating agent. This requires that the electrodes come rapidly into substantial equilibrium with the solution in immediate contact with them, and there must be stirring so thorough that the ion concentrations in the solution at the electrodes are at any instant substantially the same as in the solution as a whole. Unless these conditions are met, the electrodes will not actuate the cut-off until some excess of the titrating agent has left the buret; yet with proper calibration even this need not cause an appreciable error in the result.

An apparatus which meets the requirements, whose only source of power is the lighting circuit and a single No. 6 dry cell, was built about two years ago and proved to be satisfactory.

Description of Apparatus

The set-up, shown in Figure 1, consists essentially of two dissimilar electrodes, a vacuum-tube amplifier circuit, a solenoid-operated clamp which stops the flow of the titrating agent from an ordinary buret by pinching a short rubber tube attached to the tip of the buret, and a suitable stirrer. The potential between the electrodes is introduced into the grid circuit of the amplifying tube, and amplified so that a change of approximately 5 millivolts produces a change in the grid potential at the thyratron sufficient to cause a positive interruption of its plate current at the next alternation of its plate voltage. This interruption of the output of the thyratron deënergizes the solenoid and so closes the clamp which normally is held open by the current against a spring.

The amplifying circuit, shown schematically in Figure 2, is of the two-tube bridge circuit type (*2*) which has the advantage that the operating point at which the output voltage is zero is not affected by fluctuations in supply voltage. Since the thyratron used (*FG*-57) has a cut-off grid potential of −1 volt, and 1 volt corresponds to about 5 millivolts input, any change in the supply voltage changes the cut-off point of the circuit by much less than 5 millivolts on the electrode potential. In order to make even this error small, the voltage regulator tube maintains the somewhat critical control-grid and screen-grid potential nearly constant for a change of ±10 per cent in supply voltage.

Since some small current is drawn from the titration cell, it is advantageous to avoid the use of a constant half-cell such as the calomel or silver chloride electrode, and instead to use two dissimilar metal electrodes, both in direct contact with the titrated solution. The authors chose the electrode system, platinum-tungsten. In presence of a vanishing active ion concentration, the potential change of tungsten is usually much less than that of platinum, and so tungsten may replace the more cumbersome half-cell commonly used as a reference electrode in potentiometric titrations. The selected electrode system is readily obtained, convenient, and easy to keep in order; an occasional ignition of the platinum wire in the flame of a burner and a rubbing of the tungsten with fine emery suffices. Very little attention need be paid to the electrodes when in continuous service; but it is advisable to treat them as described if they have been in disuse for any length of time. For electrometric work generally ignition of the platinum electrode is so much the best pre-treatment to insure a sharp end point that it is wise always to employ a simple wire electrode which may easily be removed and ignited and to avoid more complex, difficult to ignite, electrodes of larger surface, such as foil sealed into glass.

The amplifying circuit is arranged to operate at any desired potential difference between the electrodes whether the difference is increasing or decreasing as the end point is passed. For a given titration this potential difference is greater on that side of the end point in which the reaction between the solution and the platinum electrode is less reversible. If the direction of the titration is toward decreased reversibility, the end point is marked by a sudden and very pronounced increase in the observed potential of the cell. This happens with many common oxidation reactions; but it does not follow that all oxidations are accompanied by a rise in potential or that the reverse is true of reductions; for, since the actual potential difference depends upon the relative reversibility of the electrode reactions on the two sides of the end point, it cannot be said that oxidation always makes for an increasing potential and reduction the reverse. In order that a reaction may serve as an analytical tool, it is necessary that the re-

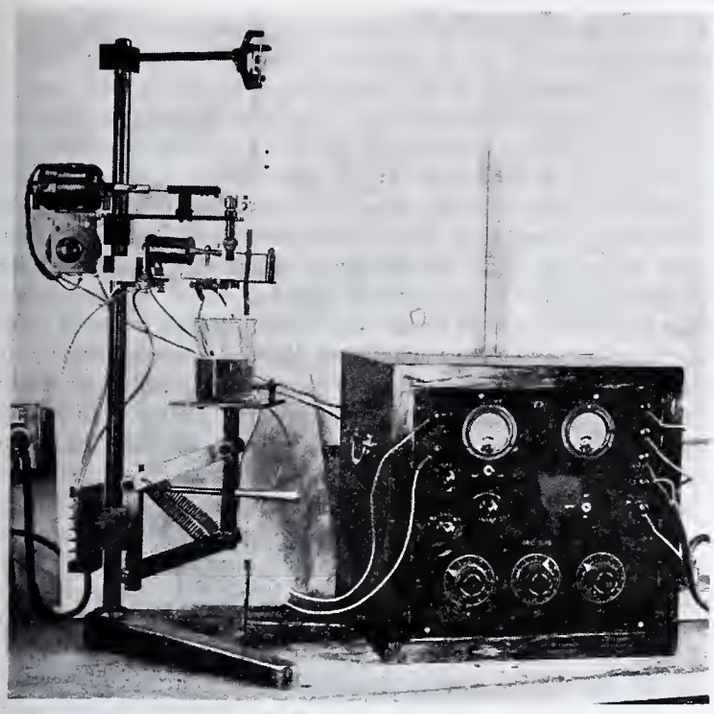

FIGURE 1. ASSEMBLY FOR AUTOMATIC CONTROL OF ELECTROMETRIC TITRATIONS

versibility of the potential of an inert electrode in contact with the titrated solution change as the end point is passed; this holds for the electrode pair adopted, which may, therefore, be used for electrometric titrations involving oxidation, reduction, neutralization, and precipitation reactions.

The instrument is set to interrupt the current to the solenoid at a definite potential. This means that the potential at the proper end point must be known for the electrode system selected, but this is not such a drawback as it may appear. On the more reversible side of the end point the observed difference in potential between tungsten and platinum is usually quite small, but in the near vicinity of the end point it changes sharply with a small added amount of the titrating solution. The precise setting of the cut-off may, therefore, vary within a considerable range without affecting appreciably the corresponding volume of the titrating solution required. The best way to ascertain the proper cut-off point for a particular titration is to plot the titration curve as obtained with the identical electrodes and a good potentiometer. The inflection of this curve, about the mid-point of the abrupt change in potential, fixes the proper cut-off. Fortunately the position of the inflection is little affected by differences in concentration of ions other than those entering directly into the titration reaction. In many cases the automatic titrator may also be set by using a color indicator, determining the cut-off potential when the color change occurs, and setting the instrument accordingly for subsequent titrations; but this is a less desirable procedure.

The method of setting the apparatus to cut off at any desired potential is quite simple, and once the setting is made it need not be readjusted unless the apparatus is shut down or a different titration is to be performed. For any particular cut-off point, say 100 mv., the procedure for adjusting and using the apparatus is as follows (Figure 2):

1. Plug in the power supply and allow the filaments to heat for 5 to 10 minutes, being sure that switch S_3 is in the "off" position.
2. Throw switch S_1 to *STD* and switch S_2 to either *INCR* or *DECR*, depending upon whether the electrode potential is increasing or decreasing at the end point.
3. Adjust potentiometer P until the voltmeter V reads 100 mv.
4. Adjust rheostat R_1 (coarse adjustment) until the plate current, as indicated by ammeter A, is within the range in which the tube is most sensitive to a change in grid voltage. This range varies with the type of the tube, the plate load resistance (R_{P1}), and the plate supply voltage. For the circuit shown a current of about 0.4 ma. is proper.
5. Close switch S_3 and adjust R_x until the pilot light just turns on. If in the course of this adjustment the plate current goes much above 0.4 ma., R_1 should be readjusted to decrease it to 0.4 ma. and then R_x reset.
6. Turn R_2 (fine adjustment) until the pilot light just goes out. The cut-off of the apparatus is now set at 100 mv. The setting may be checked by turning potentiometer P until the pilot light is illuminated and then turning P in the opposite direction until the light just goes out; the reading on the voltmeter then indicates the cut-off point and should be 100 mv.
7. With the solution to be titrated in position start the stirrer, throw switch S_1 to *TITN*, read the buret, then force open the solenoid-operated clamp to start the titration. The solenoid is purposely made too weak to open the clamp, but when the clamp is opened manually the solenoid is sufficiently powerful to hold it open as long as the solenoid is energized. The pilot lamp is illuminated whenever the solenoid is energized. The rate of flow from the buret may be controlled by the regular buret cock, but it is advisable to attach a rather fine glass tip to the lower end of the rubber tube leading from the buret. The authors found a rate of addition of the titrating solution of 1 drop (0.025 ml.) per second satisfactory. Much depends upon the efficiency of the stirring. The stirring device (shown in Figure 1), equipped with a glass stirrer with two sets of blades, was operated as rapidly as feasible within a beaker somewhat more than half full of liquid.

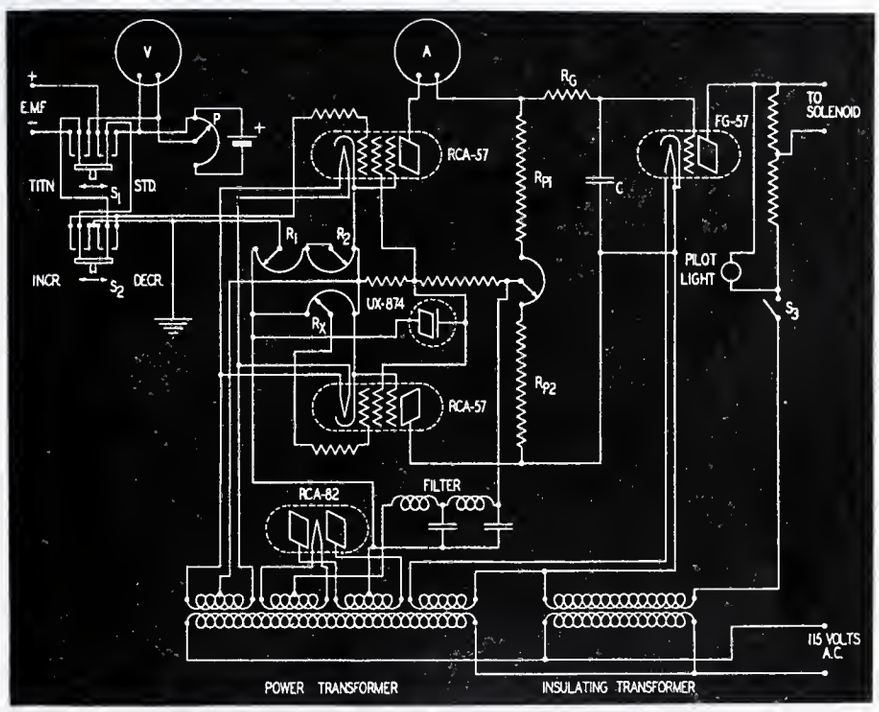

FIGURE 2. SCHEMATIC CIRCUIT DIAGRAM

V. Weston model 301 switchboard direct current voltmeter, double scale, 0 to 200 mv., 0 to 1000 mv. No. 6 dry cell placed across terminals through voltage divider
A. Weston model 301 switchboard milliammeter, 0 to 1 ma.
RCA-57. Triple-grid amplifier tube, Radio Corporation of America
UX-874. Voltage regulator tube, used here to help maintain constant the screen grid and control grid biases
FG-57. Thyratron tube, General Electric Company
RCA-82. Full-wave mercury vapor rectifier tube, Radio Corporation of America
R_1 and R_x. Rheostats of about 400 ohms; R_2 rheostat of about 50 ohms
R_G. 1-megohm fixed resistance
C. Condenser, 0.02 mfd.
Filter is composed of two 30 henry inductances and 4 mfd condensers
RP_1 and RP_2. 500,000-ohm fixed resistors; the potentiometer connected between them has 200,000 ohms total resistance
Power transformer, American Transformer Company; 4 secondaries: 2.5, 2.5, 870, and 5 volts, rating 75 va.
Insulating transformer, American Transformer Company; 1 to 1 ratio of sufficient size to supply current required by solenoid

8. When the pilot lamp goes out, the flow of reagent from the buret is cut off, and the buret is read. If the pilot lamp should happen to remain lighted though the clamp has closed, the power supply has probably been interrupted during the course of the titration, and it is necessary to open the clamp to allow more reagent to flow until the true end point is reached.

The amplifier as constructed uses 115 volts alternating current as power supply at any frequency from 25 to 60 cycles per second and, consequently, is slightly larger and heavier than would be necessary for 60-cycle operation alone. The only parts which are influenced by the frequency are the two transformers, which have to be designed for the lowest frequency that is to be used. A 25-cycle transformer will work satisfactorily at 60 cycles but a 60-cycle transformer will probably burn out at 25 cycles. The main items required are readily obtainable with the exception of the solenoid-operated clamp, which must be made. This is illustrated in some detail in Figure 3. The amplifier proper was built for about $125, exclusive of case.

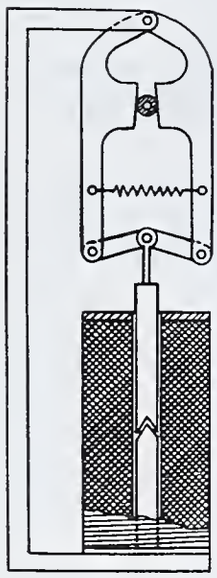

Figure 3. Detail of Clamp Actuated by Solenoid

Jaws constructed of 0.16-cm. (0.0625-inch) brass. Solenoid core about 0.925 cm. (0.375 inch) diameter.

Applications

These reactions were selected for the purpose of testing the automatic titrator—namely, the titration of Fe^{++} with potassium dichromate, of $Cr_2O_7^{--}$ with Fe^{++}, and of Zn^{++} with potassium ferrocyanide.

Titration of Fe^{++} with Potassium Dichromate. It is especially desirable to control the dichromate titration of iron automatically because it is frequently necessary to determine the iron content of a large number of samples of ores and slags under conditions that make a reasonable degree of accuracy with a minimum of skilled attention essential.

A 25-ml. portion of a stock solution of ferrous sulfate was acidified with hydrochloric acid, and the usual reduction with stannous chloride was carried out, followed by addition of mercuric chloride; it was then titrated with a 0.1 N solution of potassium dichromate (which had been recrystallized three times and dried to constant weight at 200° C.), and proved to be 0.0667 N.

The full line in Figure 4*a* is the electrode potential curve of this titration, in the near vicinity of the end point, as followed with an appropriate potentiometer; this serves to standardize the iron solution as well as to fix the proper end-point potential between the platinum-tungsten electrodes. The broken line is the curve for a similar titration, except that phosphoric acid and the color indicator diphenylamine sulfonic acid had been added. The difference in potential at the two inflections, 120 and 100 mv., is not regarded as significant for it is at most equivalent to two drops of the titrating solution. The organic color indicator does, however, lower the observed oxidation potential in presence of excess of dichromate. The true electrometric and the color end points are very nearly coincident, the former occurring just before the latter.

Table I presents typical results of a number of subsequent titrations of the stock iron solution, carried out by the automatic titrator set at the cut-off potential stated. Addition of the color indicator showed that the titrator did not stop the flow of the dichromate solution, about one drop (0.025 ml.) per second, until the latter was present in some excess; with the cut-off set at 100 mv., which is very close to the point of inflection of the titration curve, the excess was in one case as much as 0.20 ml. The over-running is due, not to any lag in the amplifying circuit, but to the fact that the attainment of complete equilibrium between the electrode system and the solution as a whole is not instantaneous, the actual lag depending upon the condition of both electrodes and especially upon the efficiency of the stirring. With the authors' set-up the error due to this lag would be negligible if the rate of flow were about one-fourth of that adopted; but a titration carried out wholly at this rate would require an hour or more, which would raise a serious question as to the practical usefulness of the automatic titrator. Indeed a question as to its usefulness arises from the fact that the point at which it cuts off is not as close to the true end point as is the color-change of the indicator. On the other hand, it is unaffected by the presence of highly colored ions, such as Cr^{+++}, Ni^{++}, and Cu^{++}, and in any case requires no attention during the whole course of the titration. Moreover, for a given set-up and a given rate of flow of the solution from the buret, the error, being substantially constant, can be brought within the limits ordinarily required in analytical work by application of a small correction, about 0.10 ml. in this case. According to the data in Table I, the error was reduced somewhat by setting the cut-off at 75 mv., and became negative with the cut-off set at 50 mv.; it may therefore be partly taken care of by setting the circuit to actuate the cut-off somewhat in advance of the potential difference at the true end point as determined by preliminary titration with a good potentiometer. In a series of similar titrations, therefore, the use of the automatic titrator would yield results of sufficient accuracy with a great saving in time and attention required on the part of a skilled operator.

Titration of $Cr_2O_7^{--}$ with Fe^{++}. The titration of $Cr_2O_7^{--}$ with Fe^{++} is the reverse of the titration just discussed. The color indicators of the diphenylamine group cannot be added to the dichromate solution because they are destroyed by the strong oxidizing agent; so that it is necessary to add an excess of Fe^{++}, then the indicator, and to determine the excess Fe^{++} with a standard solution of potassium dichromate. This complication is avoided by the use of the automatic titrator. Figure 4*b* shows the end-point curve of two typical titrations of the standard dichromate solution; the solutions as titrated contained about 20 per cent by volume of reagent hydrochloric acid. The potential change in the near vicinity of the end point is much larger for a given increment of the titrating solution than is the case for the reverse titration. The mean of several titrations in close agreement showed the Fe^{++}

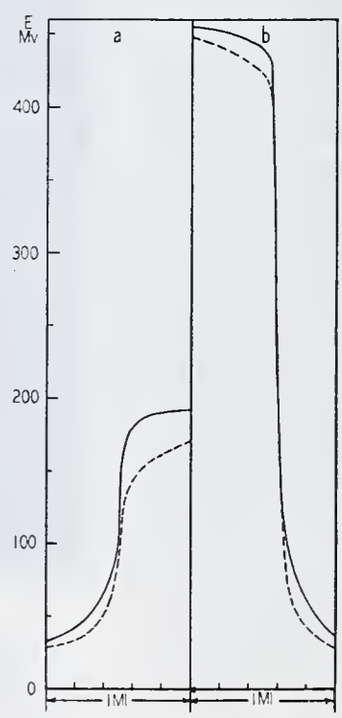

Figure 4. Electrode Potential Curve in Near Vicinity of End Point for Titration of:

(*a*) Fe^{++} solution with 0.1 N $Cr_2O_7^{--}$ solution; full line, color indicator absent; broken line, color indicator present; (*b*) $Cr_2O_7^{--}$ solution with 0.1 N Fe^{++} solution; two typical titrations

TABLE I. TITRATION OF Fe^{++} WITH 0.1 *N* POTASSIUM DICHROMATE

(True end point at 16.68 ml.)

Cut-off Setting	Volume Shut Off Automatically	Error
Mv.	Ml.	Ml.
100	16.66	−0.02
100	16.84	+0.16
100	16.86	+0.20
100	16.84	+0.16
75	16.76	+0.08
75	16.61	−0.07
75	16.81	+0.13
50	16 62	−0.06
50	16.61	−0.07

TABLE II. TITRATION OF $Cr_2O_7^{--}$ WITH Fe^{++}

Cut-off Setting	Volume 0.1 *N* $K_2Cr_2O_7$ Taken	Equivalent Volume 0.1 *N* FeSO Shut off Automatically	Error
Mv.	Ml.	Ml.	Ml.
350	20.00	20.04	+0.04
	20.00	20.05	+0.05
	20.00	20.09	+0.09
	25.00	25.10	+0.10
	25.00	25.14	+0.14
300	20.00	20.15	+0.15
	20.00	20.10	+0.10
	20.00	20.09	+0.09
	30.00	30.02	+0.02
250	20.00	20.04	+0.04
	20.00	20.10	+0.10
	20.00	20.16	+0.16
	20.00	20.15	+0.15
	20.00	20.16	+0.16
100	20.00	20.21	+0.21

solution (not the same solution referred to above) to be 0.0669 *N*, and the end-point inflection to lie close to 250 mv.

Table II presents the data obtained with the automatic titrator. A considerably greater range in the setting is permissible than with the reverse titration, as the curves indicate. A setting of 100 mv. is, however, clearly too low; the error with the higher settings is not serious but always positive.

DETERMINATION OF ZINC WITH POTASSIUM FERROCYANIDE. The volumetric determination of zinc with potassium ferrocyanide is particularly suited to the automatic titrator because the reaction is inherently slower than most of those utilized by the analyst. The rate of addition of the titrating agent may therefore be several times as fast as that ordinarily used, and the titrator will stop the flow 1 to 2 ml. before the true end point by virtue of a temporary accumulation of ferrocyanide. The pilot lamp relights a few seconds after the cut-off is made. By manipulating the buret cock the rate of flow of the titrating solution is reduced to less than 1 drop per second, the clamp is reopened, and the titration completed. Much time is saved by this procedure.

A standard solution of zinc was prepared by dissolving zinc metal distributed by the Bureau of Standards for use in thermometry (99.993 per cent Zn) in hydrochloric acid. The solution as prepared contained 0.01084 gram of zinc per ml. Samples of this solution were titrated electrometrically with a solution of potassium ferrocyanide at 65° C. To each sample 13 ml. of reagent ammonia and 3 ml. of excess hydrochloric acid, methyl orange serving as the indicator, were added before titrating. Figure 5 gives the end-point curve of two typical titrations; 400 mv. was adopted as the end-point potential. One milliliter of $K_4Fe(CN)_6$ was found equivalent to 1.034 ml. of Zn^{++} from the titration curves.

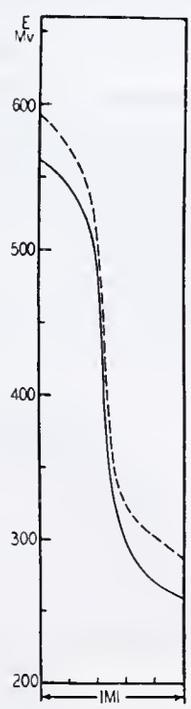

FIGURE 5. ELECTRODE POTENTIAL CURVES IN NEAR VICINITY OF END POINT

Two typical titrations of a zinc solution with potassium ferrocyanide

The titrations made with the automatic titrator, which are listed in Table III, were also made at 65° C. The results for this ordinarily rather troublesome titration are regarded as favorable.

TABLE III. DETERMINATION OF Zn^{++} WITH POTASSIUM FERROCYANIDE

Cut-Off Setting	Volume Zn^{++} Solution Taken	Equivalent Volume $K_4Fe(CN)_6$ Shut Off Automatically	Error
Mv.	Ml.	Ml.	Ml.
400	20.00	20.14	+0.14
	20.00	20.11	+0.11
	20.00	20.04	+0.04
	50.00	50.22	+0.22
	50.00	50.17	+0.17
	50.00	50.18	+0.18

It may be pointed out that on all the titrations cited a correction of −0.10 ml. applied to the buret reading at the close of the titration brings the error involved within acceptable limits for most analytical work. This correction is largely a function of the authors' working conditions, particularly of the rate of addition of the titrating solution and the effectiveness of the stirring.

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(1) Müller and Partridge, IND. ENG. CHEM., 20, 423 (1928).
(2) Nottingham, *J. Franklin Inst.*, 209, 287 (1930).

RECEIVED March 19, 1935.

Busy Year Planned by the Paper Section of National Bureau of Standards

With the assistance of funds from other government agencies and from outside organizations, the paper section of the National Bureau of Standards expects to expand its research activities during the ensuing year.

A new project recently initiated is a study of the possible effect on papers of fumigating gases used to rid written and printed materials of destructive insects. This was undertaken at the request of the National Archives and with their financial assistance.

A new venture, which will take the section into a new field, is a study of the stability of prints contained on motion picture films. This form of record material has assumed great importance, librarians, educators, and others interested in the spreading of knowledge and in preserving it being deeply interested in the possibilities of film records.

With the assistance of a fund granted for the purpose to the National Research Council by the Carnegie Foundation, it is planned to make a year's study of the resistance of the film records to various degrees of temperature, humidity, and light. It is hoped that this work can later be expanded into a comprehensive study of the many other problems concerning miniature records, and of problems related to sound recordings.

Direction of the participation in the standardizing activities of the T. A. P. P. I. Paper Testing Committee will be continued. The committee has developed 37 standard testing methods and has 14 more under development at the present time. Additional testing work consists of an attempt to develop a device for measuring in numerical terms the rate of failure of printed currency under conditions that produce appearance and loss of strength similar to those caused by actual service wear. This work is supported by the Treasury Department.

Determination of Water and Hydrogen Sulfide in Gas Mixtures

FOSTER FRAAS and EVERETT P. PARTRIDGE

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IN TRANSFERRING gas mixtures at atmospheric pressure from their containers to an apparatus for analysis the use of a displacing liquid may cause the loss of a condensed constituent, while certain constituents may react with mercury and thereby prohibit the use of an evacuating pump containing this liquid. The problem in both cases can be solved by utilizing the evacuation method if proper absorbents are placed between the pump and the gas container to remove the interfering constituents and allow their quantitative determination. Absorption of this type at constantly diminishing pressure gradually decreases in efficiency as lower pressures are approached, owing to the fact that the partial pressure of each nonabsorbable constituent constantly diminishes while the partial pressure of each absorbable constituent over its absorbent remains substantially constant. In such a case the net absorption between a given set of pressure limits, rather than the specific absorption at any particular pressure, determines the accuracy of the analysis. This paper presents an apparatus and procedure for the analysis of gas mixtures containing water vapor and hydrogen sulfide, which are typical examples of gases having the interfering properties of condensability and reactivity with mercury. The method, however, is general and may be applied to a variety of other gases.

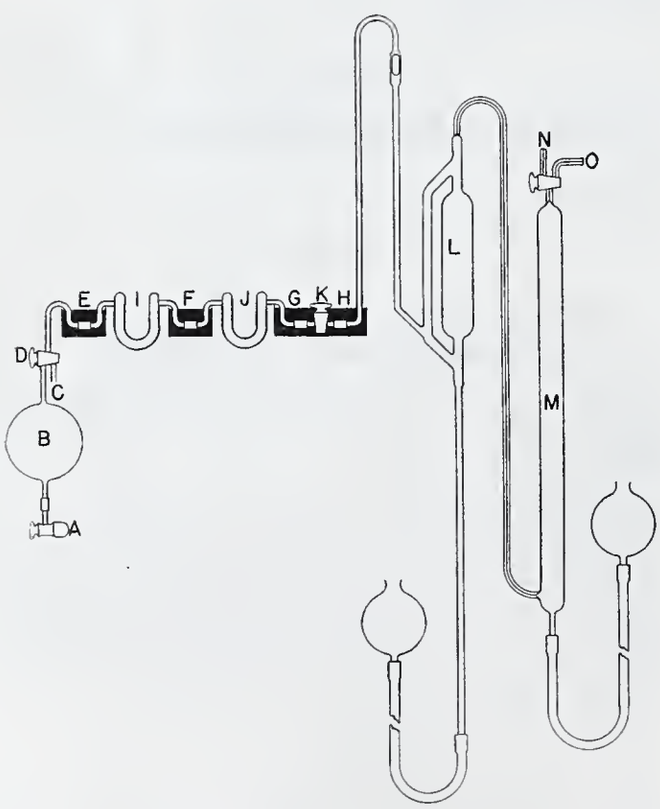

FIGURE 1. LAYOUT OF ABSORPTION SYSTEM

A. Water sample bulb
B. Air and hydrogen sulfide sample bulb, 200 cc. capacity
C. Flushing aperture used in filling sample bulb
D. Three-way cock
E, F, G, H. Mercury-immersed rubber tube connections. Glass tubing meeting end to end inside thin rubber tubing
I, J. Absorption bulbs for water and hydrogen sulfide, respectively
K. Two-way cock
L. Töpler pump, 200-cc. chamber
M. Gas reservoir, 230 cc.
N. Vent
O. Connection to Orsat gas analysis apparatus

Apparatus

The apparatus used with this method of analysis, as shown in Figure 1, consists of a Töpler pump connected to the sample bulb with the necessary absorption tubes intervening between the pump and sample bulb. The volume of the absorption tubes should be as small as consistent with the use of an adequate amount of absorbent.

Method of Operation

The procedure is essentially to evacuate the system up to stopcock D, to allow the sample bulb gas to fill the absorption system slowly up to stopcock K, and then to complete the evacuation, collecting the nonabsorbed gases in reservoir M. The volume of the dry nonabsorbed gases is determined in the buret of an Orsat apparatus. Absorption tubes I and J are filled with dry air through a drying tube containing magnesium perchlorate attached to stopcock K at H. They are then disconnected and weighed, after being carefully wiped free of mercury from the immersion seals. No difficulty will be encountered in removing this mercury if it is clean, preferably freshly distilled, and if a small camel's-hair brush with fairly stiff bristles is used. The motion of the brush should be short and jerky. The absorption tubes are always weighed with their rubber connections removed. Between absorptions and weighings the openings are closed by rubber connections into which are inserted small glass rods.

Accuracy of Analysis

The most significant sources of error may be classified as (1) error due to the imperfect absorption as the sample is being evacuated, (2) error due to deabsorption of the absorbent during the first evacuation of the absorption tubes, and (3) error due to the fraction of the sample not removed by evacuation.

For the removal of infinitesimal portions of gas with a pressure change, $-dP$, the amount of absorbable gas lost by nonabsorption in each portion is represented by the equality:

$$dN_A = \begin{matrix}\text{total moles}\\ \text{nonabsorbable}\end{matrix} \times \begin{matrix}\text{fractional}\\ \text{pressure change}\end{matrix} \times \frac{\text{pressure of absorbable gas}}{\text{pressure of nonabsorbable gas}}$$

It follows that:

$$\frac{N_A}{N_N} = 2.3\,\frac{P_A}{P_1}\log\frac{P_1}{P_2} \qquad (1)$$

where

P_1, P_2 = initial and final partial pressures of the nonabsorbable gas

P_A = constant partial pressure of the absorbable gas over the absorbent

N_A = moles of absorbable gas not absorbed after passing over the absorbent

N_N = moles of nonabsorbable gas in bulb at pressure P_1

Provided the absorbable component does not constitute the major portion of the gas and the volume of the absorp-

tion tubes is only a small fraction of the total volume, P_1 may be calculated from the volume of the sample bulb.

The error due to deabsorption of a reversible adsorbent during the first evacuation of the absorption tubes is small, as is shown by an application of Equation 1.

Corrections for the incomplete evacuation of the sample bulb can be made to the analyzed values of the proper constituents. When the ratio of the initial and final pressures is of sufficient magnitude, this correction is omitted.

TABLE I. ANALYSIS OF KNOWN GAS MIXTURES

Analysis	Actual Air, S.T.P. Cc.	Actual H_2S, S.T.P. Cc.	Actual H_2O Gram	Analyzed Air, S.T.P. Cc.	Analyzed H_2S, S.T.P. Cc.	Analyzed H_2O Gram	Final Pressure of Evacuation, Mm. Hg
1	197.5	0.0	0.0000	197.2	−0.3	0.0004	5[a]
2	157.0	41.2	0.0000	156.9	40.8	0.0000	5[a]
3	158.5	40.2	0.1035	159.0	40.1	0.1038	1
4	166.8	31.6	0.0980	166.0	31.3	0.0978	1

[a] Values corrected for residual gas in sample bulb.

An absorbent for hydrogen sulfide which carries a very low partial pressure of the gas above it and which is very selective in the presence of many other gases is partly dehydrated copper sulfate pentahydrate. The use of this reagent as an absorbent for hydrogen sulfide was originated by Fresenius (*1*, *2*), who recommended the dehydration for 4 hours at 150° to 160° C. of copper sulfate absorbed from solution by pea-sized pumice. For the present work it was found better to omit the pumice and to dehydrate 10- to 20-mesh particles of the pentahydrate for the same time at this temperature. Part of the reagent space on the exit side of the absorption tube should be filled with anhydrous calcium chloride to recover any water removed from the copper sulfate.

Since it was impossible to employ calcium chloride as a drying agent for gases containing hydrogen sulfide, magnesium perchlorate (anhydrone) was used in *I*, the absorption tube for water vapor. An appreciable dehydration of the copper sulfate absorbent is the only objection to the use of magnesium perchlorate. Using these reagents, the method was checked with samples of gas of known composition.

Samples of gas containing known amounts of air, hydrogen sulfide, and water vapor were prepared in bulbs *B* and *A* of Figure 1. Bulb *A* provided with a stopcock contained the water for the sample, and when evacuated and weighed before and after the addition of water gave the known amount of water. It was attached to bulb *B* with rubber tubing sealed with Duco cement. Bulb *B* was then evacuated and filled with known amounts of air and hydrogen sulfide calculated from the known volume of the bulb and the pressure changes measured on a mercury manometer. A small-bore tube connected the manometer with bulb *B;* since the air was introduced into the bulb first and the hydrogen sulfide last, little or no hydrogen sulfide reacted with the mercury in the manometer. Outlet *C* provided by the three-way cock served for flushing purposes in filling the bulb.

The hydrogen sulfide was prepared from iron sulfide and hydrochloric acid and washed by bubbling through potassium hydroxide saturated with hydrogen sulfide. Prepared in this manner it did not contain hydrogen or hydrocarbon impurities, since the determined and actual values for air or nonabsorbed gas in the analysis of mixtures of air and hydrogen sulfide checked as well as in the analysis of air alone. Both the air and the hydrogen sulfide were dried over phosphorus pentoxide before being introduced into bulb *B*.

Analyses of the samples are shown in Table I. The residual air after absorption of the water and hydrogen sulfide was measured volumetrically with the customary corrections for temperature and pressure. The deviation of the determined values for water vapor from the actual varies from +0.0004 to −0.0002 gram. The partial pressure of water vapor over magnesium perchlorate is considerably less than 0.1 mm. (*4*), so that the variations that do occur are caused by the limitation of the gravimetric determination of the absorbed water rather than by the limitation of the absorption.

The calcium chloride at the exit end of the copper sulfate tube should maintain in the gases leaving this tube a partial pressure of water vapor around 0.3 mm. (*3*). Assuming that the gases entering the copper sulfate tube are absolutely dry, then the amount of water picked up by these gases and lost from the copper sulfate tube may be calculated by means of Equation 1 as a negative absorption of hydrogen sulfide. This calculation gives for all four analyses the value of −0.2 cc. The actual deviations are −0.3, −0.4, −0.1, and −0.3 cc., respectively. Although the determination of hydrogen sulfide is not as accurate as that of water vapor and air, the method is not condemned, since other absorbents may be chosen. The use of this particular reagent was decided upon because of its selectivity in the presence of a variety of gases, so that it was quite possible to analyze mixtures of gases containing in addition hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, and ethylene.

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(3) McPherson, A. T., *J. Am. Chem. Soc.*, **39**, 1317–19 (1917).
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Buret Assembly for Standard Reducing Solutions

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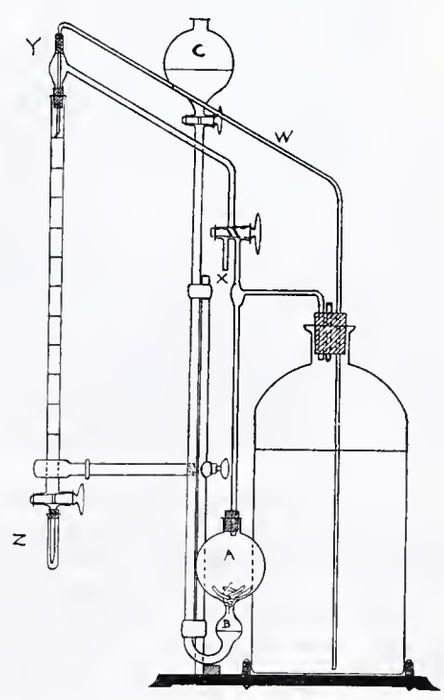
STANDARD solutions of reducing agents—for example, titanous and ferrous salts—are required for certain volumetric determinations. They have the disadvantage of rapid deterioration unless the air remaining in the storage bottle is replaced by an inert gas. Various assemblies of apparatus for their preservation and delivery at full strength have been suggested, but the writer has seen none which seems to present all the advantages of the form sketched.



A standard buret is used, readily detached for cleaning. The automatic zero-point arrangement is easily adjusted and is reliable. The solution does not come in con-

tact with rubber. It is constantly under pressure of inert gas, but the necessary connections are of such nature that chance of loss of either solution or gas from leaks is remote. The assembly is portable and may be set in a cupboard when not required.

The gas generator, *ABC*, was made from the bulbs of two 250-ml. separatory funnels sealed to a length of heavy tubing in which a 100-ml. bulb had been blown, and bent as sketched. This bulb, *B*, is essential, as it takes care of changes in gas volume from variations in temperature and pressure as well as excess gas evolved from dilute hydrochloric acid adhering to the zinc sticks or marble fragments in *A*. *ABC* is attached to the rod of the retort stand on which the apparatus is assembled by wrappings of friction tape. The container for solution may be a 2.5-liter acid bottle, which is prevented from shifting on the rectangular iron base of the support by four rubber-protected bolts.

Part *Y* supplies inert gas to protect the solution while in the buret, and is slightly tapered below to expand a soft-rubber sleeve within the mouth of the buret, making a secure connection. The siphon tube for solution passes through *Y*, and is attached to it at the top only; the joint is made gas-tight with soft de Khotinsky or similar cement, permitting precise adjustment of the zero point by warming to soften the cement. The space within *Y* below is open, to allow gas to enter the buret freely. It is important that the vertical part of the siphon tube at the top be quite narrow and no longer than necessary, to insure satisfactory performance; the slight bend at the tip directs the stream against the wall of the buret, avoiding bubbles.

To fill the buret, stopcock *X* is turned to release gas, while at the same time gentle suction may be applied to a rubber tube (not shown) attached at *X*; excess pressure in the bottle then forces the solution through the siphon. When the buret is filled to slightly over the zero point, stopcock *X* is reversed to readmit the inert gas; equalization of the pressure in buret and bottle then permits excess solution to siphon back into the bottle, leaving the buret filled just to the zero point, ready for the titration. The bottle may be refilled through the opening in the stopper shown plugged by a piece of rod, without disturbing any other connection. This opening also serves to vent the bottle when displacing air by gas after filling. The sleeve, *Z*, on the tip of the buret contains a little of the solution, and prevents stoppage by crystallization if in place while the buret is not in use.

Every set-up of this type is open to the criticism that evaporation from the surface of the solution in the bottle, with condensation on the walls above, results in a lack of uniformity in the solution. This apparatus is not so heavy that it cannot be shaken as a unit to remix the solution, but there is also danger that on long standing water vapor may diffuse into the gas generator and thus be permanently lost from the bottle. A layer of pure paraffin oil just sufficient to cover the solution is an effective remedy; the only objection is the fact that oil appears to contain dissolved oxygen, so that the titer will decrease for several days after the first filling, unless the oil has been given a thorough preliminary treatment with the same reagent.

Received March 22, 1935.

Note to Authors

IN THE preparation of manuscripts authors should address themselves to specialists in their particular fields, rather than to the general reader. If the article describes a new method, the author should endeavor to tell the complete story, so that the reader will not have to wait for succeeding contributions or duplicate the unpublished tests in order to find out whether he can apply the method in his own work.

The following is suggested as a general outline to be followed in preparing analytical methods for this edition:

1. Preliminary statement or introduction, in which the need for the method should be stated, brief reference to other methods or literature given, etc.
2. Experimental:
   - Outline of proposed method
   - Description of apparatus and reagents
   - Procedure
   - Data:
     - Interfering substances or conditions
     - Concentration range through which the method is applicable
     - Accuracy of the method
     - Precision of the method
3. Discussion and summary

The author should state at the outset why he thinks the paper is worth publishing. If it deals with a method of analysis, he should give some comparison with established methods in point of speed, applicability, accuracy, and cost. Extensive reviews of the literature should not be given and such references as are cited should be carefully checked. Incorrect references are inexcusable and cast doubts on the author's reliability. The theoretical considerations on which the method is based should be clearly set forth.

In the experimental part, previously published or well-known procedures which have been followed should only be designated or references given to them. If, however, the method is new, the data upon which it is based should be presented but in no greater detail than is necessary to prove its soundness. New procedures should be clearly described, that readers can easily duplicate the work. Loose directions should be avoided, unless the author knows that no possible harm can result from the most liberal interpretation that can be made of such expressions as "to the faintly acid solution," "wash the precipitate," "ignite," etc. If new or uncommon reagents are needed, the author should state their probable cost, where they can be purchased if rare, or how they can be prepared, if not on the market.

The author should distinguish carefully between precision and accuracy. Briefly but somewhat roughly stated, accuracy is a measure of degree of correctness; precision is a measure of reproducibility. The precision of a result does not necessarily have anything to do with its accuracy; it serves merely as a measure of the duplicability of the procedure in the hands of a given operator. No claim for accuracy should be made unless the author believes that he has satisfactorily established the correct result.

The author should be frank and define the limitations of the method. Tests dealing with the effects of foreign compounds should be made on mixtures in which the ratios of the compounds sought to the foreign compounds are varied and simulate conditions that are likely to be encountered in practice. If the author has made no such tests, he should state that he has no knowledge of the effects of foreign substances. It is desirable that possible applications of methods should be stated.

A summary or prefatory abstract should acquaint the reader with the main points of the article. This should give concisely where possible the substances determined, nature of material to which determination is applicable, interfering substances, range of concentration to which method is applicable, whether or not a sensible constant error is involved—that is, the accuracy of the method—and its precision. Either the summary or the prefatory abstract is so often used by abstractors that the author may well spend considerable time in their preparation, in order to be certain that proper emphasis is given to the main features of the contribution.

Our "Suggestions to Authors" is available to those unfamiliar with the form of manuscript and illustrations preferred by Industrial and Engineering Chemistry.

Manometric Manostat

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THE apparatus here described has been used successfully by the writer for controlling pressures between one and 850 mm. It is particularly convenient for maintaining a given pressure either below or slightly above atmospheric pressure during distillations.

The electrical circuit used is that of Hershberg and Huntress (*1*). The manometer, which is made of 8-mm. tubing, is provided with a 1-mm. stopcock at the bottom and an ordinary stopcock at the top of the open arm. There are also two platinum wire contacts, P_1 and P_2, on the open arm. Contact P_1 is conveniently located about 12 cm. from the bottom bend in the manometer tubing and should be sharpened to a fine point. The meter stick is set in such a position that the 10-cm. mark is exactly level with the tip of contact P_1, for convenience in making readings. Relay A (2000-ohm telephone relay) is fixed to a carriage which is moved by means of a screw, from leak L_1 to leak L_2. The leaks consist of ordinary needle valves soldered at the open end to 2-cm. long brass rods through which fine holes 0.05 cm. (0.02 inch) have been drilled. Stopcock S_1 serves to admit or remove mercury from the manometer, stopcock S_2 to close off the leaks completely if desired, and stopcock S_3 to fix the volume of air in the otherwise open arm of the manometer.

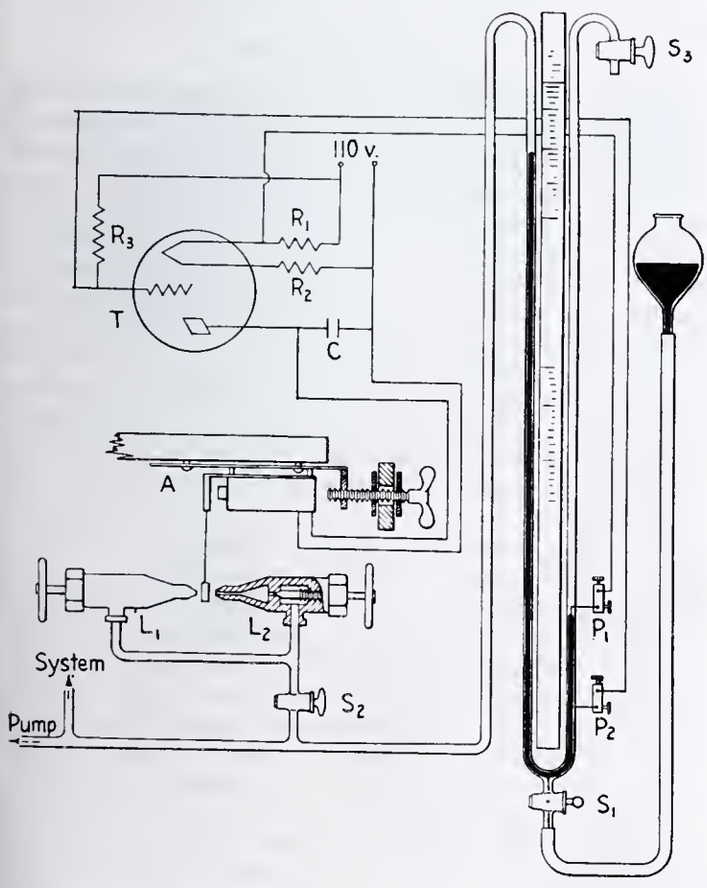

FIGURE 1. DIAGRAM OF APPARATUS

Resistance R_1 is a 40- to 60-watt lamp, R_2 a 25- to 40-watt lamp, and R_3 a 3- to 5-megohm resistance of 2-watt capacity. Condenser C is of 5 mfd. rating. T is a 71-A vacuum tube. All of the apparatus, exclusive of the manometer, may be easily mounted in a box 25 × 15 × 15 cm. (10 × 6 × 6 inches) with the controls placed conveniently on the outside.

The operation of the apparatus is simple. If it is desired to maintain a pressure below atmospheric pressure, S_3 is opened, the pump is started, and the amount of mercury in the manometer is adjusted by means of the leveling bulb so that the difference in height between the two mercury levels subtracted from the barometric pressure gives the pressure desired. Introducing more mercury into the manometer increases the degree of vacuum attained. Removing mercury has the reverse effect. The relay is set so that its armature operates against L_2. L_1 may then be used as an auxiliary leak. As soon as the desired pressure is attained, S_3 is closed to prevent changes in the atmospheric pressure from influencing the controlled pressure.

If it is desired to operate at pressures above atmospheric, the vacuum pump is replaced by an air-pressure pump and the relay is set to operate against L_1. In this case L_2 may be used as an auxiliary leak. The height of P_1 above the lower end of the meter stick determines the amount of pressure above atmospheric that may be controlled. Ordinarily this will not need to be more than 30 or 40 mm. if the object in view is to maintain a pressure of 760 mm. However, at high altitudes or for other reasons it may be desirable to maintain an increased pressure of several hundred millimeters over the prevailing atmospheric pressure. In such cases P_1 must be fixed in the manometer tube at a correspondingly higher level or a third contact introduced. As soon as the desired pressure is attained S_3 is closed.

Advantages of Manometric Manostat

Except for the electrical control, which may be much simplified (*2, 3*), the apparatus is relatively inexpensive. The glass parts may be easily put together by an amateur glass blower.

All pressures from a few millimeters to 100 mm. or more above the prevailing atmospheric pressure may be controlled with an accuracy of ±0.2 mm. or less. Changes in the controlled pressure due to changes in the atmospheric pressure are avoided.

The settings are rapidly and easily made.

A closed-arm manometer which will eventually become inaccurate with frequent operation is avoided.

The manometer is easily drained, cleaned, and refilled through S_1.

Chief Disadvantages

Like all constant-volume pressure controls, the manometric manostat is subject to ambient temperature variations. These may be avoided or corrected for by surrounding the open arm of the manometer with a tube filled with water in which is immersed a thermometer according to the manner prescribed for burets used in gas analysis.

The apparatus is subject to the disadvantages inherent in all manostats using mercury as the contact liquid (*1*). In the writer's opinion these disadvantages are not as great as those which arise from the use of other liquids, such as sulfuric acid which rapidly absorbs organic vapors and water and hence must be renewed frequently.

Literature Cited

(1) Hershberg and Huntress, IND. ENG. CHEM., Anal. Ed., **5**, 144, 344 (1933).
(2) Jacobs, *Ibid.*, **7**, 70 (1935).
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RECEIVED January 26, 1935.

Determination of Traces of Hydrogen Sulfide in Sewer Gases

A Convenient Field Method

W. J. WILEY, Government Chemical Laboratory, Brisbane, Australia

IN THE course of a recent investigation of a sewage system it became necessary to make a large number of determinations of the concentration of hydrogen sulfide in the sewer gases. As the sewer was about 20 meters (60 feet) below ground level and determinations at numerous different places were to be made on the same day, it was desirable that an apparatus be devised that would obviate the necessity of the manipulator's descending the manholes and would be strong and rapid in use. The concentrations of hydrogen sulfide to be measured varied from about 0.1 to 30 parts per million. A high degree of accuracy in the measurements was unnecessary. The apparatus and method described were found to cover all the requirements, and when used in the field gave results with an accuracy of at least 10 per cent of the quantity measured.

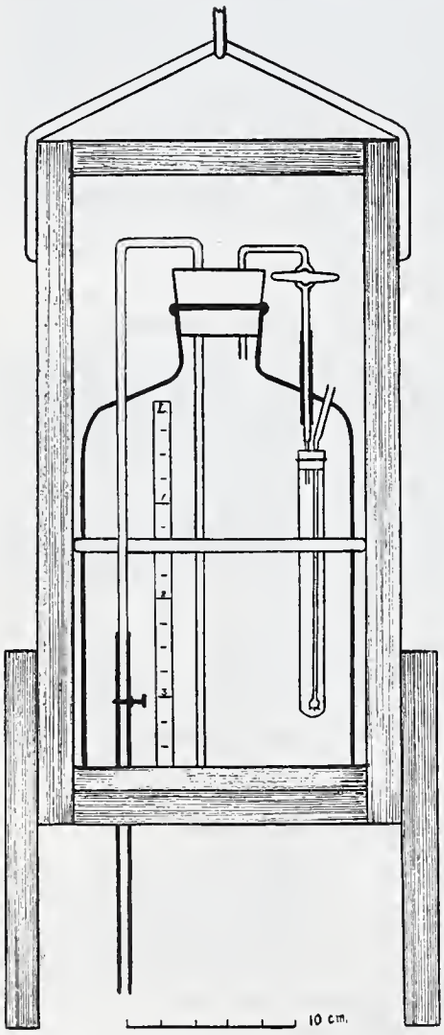

FIGURE 1

The principle of the method employed was the absorption of the hydrogen sulfide in potassium hydroxide and its colorimetric determination, using potassium plumbate and a series of comparison tubes containing dye solutions prepared so as to correspond to various concentrations of the gas.

Apparatus

The apparatus (Figure 1) consisted of a graduated 4-liter Winchester bottle which with a siphon acted as an aspirator. This drew the gases through an absorption tube consisting of a 15 × 1.3 cm. test tube with a mark etched at a height corresponding to 10 cc. This was filled to the mark with 5 per cent potassium hydroxide solution. The bubbling tube terminated in a bulb having three small orifices, so that the gas divided into three fine streams of bubbles. A glass tap regulated the rate of flow of gas through the absorption tube. A rubber band made from stout tubing circled the aspirator bottle and served the dual purpose of holding the absorption tube and acting as a cushion for the bottle in its case. This case was three-sided and stoutly constructed of wood, so as to be a neat fit for the bottle. The front was left open except for a small ledge to prevent the bottle sliding forward. The siphon tube ended with a length of rubber tubing which slipped through a hole in the base of the case. The height of the case was just sufficient to enable the aspirator to be lifted over the ledge for removal for refilling with water. Extensions to two sides of the case enabled it to be placed on the ground without interfering with the action of the siphon. Thirty-three meters (100 feet) of plaited cord were attached to the case so that it could be lowered down a manhole.

A case similar to that used for some types of portable pH colorimetric apparatus was used to hold the comparison tubes, a bottle of 5 per cent potassium hydroxide and one of potassium plumbate, and a stock of absorption tubes, as these were used for only one determination before being washed.

Standardization

Owing to the rapidity with which the lead sulfide coloration fades, resort was had to more permanent color standards prepared from dye solutions. No single dye having the same tint as the lead sulfide was found, but a good match could readily be obtained by using a mixture of red, yellow, and blue dyes. Those selected were Ponceau 3 R, Chlorozol fast yellow, and Cotton blue (B. D. H.). No special virtue is claimed for these, other than that they were found reasonably stable to light and slight changes of pH in the solution and happened to be readily available. It was found that 30 drops of 0.1 per cent Chlorozol yellow, 5 drops of 0.1 per cent Ponceau 3 R, and 8 drops of 0.1 per cent Cotton blue diluted to 100 cc. gave a coloration, when compared in the absorption tubes of the apparatus, of similar tint and intensity to a solution containing 14×10^{-6} grams of hydrogen sulfide dissolved in potassium hydroxide and treated with 5 drops of potassium plumbate. At 25° C. and barometric pressure this would correspond to 10 parts per million of hydrogen sulfide if 1 liter of sewer gas had been aspirated through the absorption tube. In preparing the standards 25° C. was taken as typical of working conditions and no attempts were made to correct for changes of temperature and pressure. A series of standards was prepared in uniform tubes identical with that used for absorption of the hydrogen sulfide and of intensities corresponding to 0, 0.5, 1, 2, 4, 6, 8, 10, 12, 16, and 20 parts per million of hydrogen sulfide in the gas if 1 liter were aspirated. The color corresponding to 0.5 part per million when the tube was examined longitudinally against a white base was quite definite. In preparing these standards comparison was made with sodium sulfide solutions carefully analyzed by titration with iodine and thiosulfate and added to 5 per cent potassium hydroxide, the color being developed with 5 drops of potassium plumbate in an identical manner to that used in an actual determination.

The color of a dye standard was measured with a Lovibond tintometer and it was found that after one month in the diffused light of the laboratory it had not changed. However, the standards used were exposed to light only when a comparison was being made.

In order to be sure that the simple absorption tube used was effective, mixtures containing 5 and 15 parts per million of hydrogen sulfide in air were prepared in an apparatus similar to that described by Truesdale (*1*). These were aspirated at the rate of 1 liter in 10 minutes through the absorption tube. On adding potassium plumbate, the color developed was immediately matched with the previously prepared dye standards and found to correspond with a practically complete absorption of the hydrogen sulfide.

Determination

The determination on the field was simple and rapid. The siphon was started and the sampling apparatus immediately lowered down the manhole to within 30 cm. (1 foot) of the sewage. After 10 minutes, when 1 liter of the gas had been aspirated, it was brought to the surface, the absorption tube was removed, 5 drops of potassium plumbate were added to its contents, and the color was immediately compared with the dye standards. The total time involved, including packing and unpacking, was generally less than 15 minutes at any particular place. When the concentration of hydrogen sulfide was lower or higher than corresponded to the standards, a larger or smaller quantity of the gas was aspirated through the apparatus.

Acknowledgment

The author's thanks are due to J. B. Henderson, Queensland Government Analyst, for permission to publish this description.

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(1) Truesdale, E. C., Ind. Eng. Chem., Anal. Ed., 2, 299 (1930).

Received March 15, 1935.

A Direct-Reading pH Meter for Glass, Quinhydrone, and Hydrogen Electrodes

ALLAN HEMINGWAY, University of Minnesota Medical School, Minneapolis, Minn.

THE glass electrode is rapidly replacing the hydrogen and quinhydrone electrodes. It reaches equilibrium very rapidly, there being no drift due to "poisoning." It is not affected by oxidizing-reducing substances, and is applicable through a wide pH range of 0 to 11.5. There is no removal of dissolved gases, such as carbon dioxide, due to the bubbling of hydrogen through the solution whose pH is to be measured. One difficulty with the glass electrode has been that the high resistant membrane makes balancing of the opposing e. m. f. from a potentiometer a difficult operation, since the high resistance of the glass reduces the balancing current to a small value. Another difficulty is that when a continuous current is drawn from a glass-electrode system the membrane polarizes, changing its equilibrium potential.

In order to eliminate these difficulties several schemes (*1*) have been suggested. One which possesses certain inherent advantages is the method, first suggested for glass electrodes by Morton (*2*), in which the variable known e. m. f. from a potentiometer, the glass-electrode assembly, and a high-grade condenser are in series, the potentiometer e. m. f. opposing the cell e. m. f. in the usual way. The condenser is charged to the difference of potential between the potentiometer and the glass electrode. By means of a suitable tapping key the condenser is discharged through a voltage amplifier with a ballistic galvanometer in the plate circuit of the last tube. When the voltage of the glass-electrode assembly is balanced by an equal e. m. f. from the potentiometer, the ballistic discharge is zero. A small residual e. m. f., due to grid current, can be made negligibly small by a suitable choice of tube, grid resistance, and grid condenser (*3*)

Improvements of this new circuit over one previously described (*1*) consist in the use of alternating current vacuum tubes whereby storage batteries are eliminated. Vacuum tubes of higher amplification are used, with the result that an inexpensive portable microammeter replaces the type R galvanometer. The temperature-correction device, whereby the potentiometer is converted into a pH meter for any temperature, and the accessory potentiometer as well as the connections for quinhydrone and hydrogen have necessitated complete redesigning and revising of the circuit.

Construction of Meter

The ballistic principle has been utilized in a direct-reading pH meter designed for rapid and simplified measurements (Figure 1).

The upper circuit is a Leeds & Northrup potentiometer of the student type. The variable voltage is obtained from a variable decade of nine 40-ohm coils and a 40-ohm slide wire. When balanced as a simple potentiometer with the standard cell, there is a 100-millivolt potential drop across each 40 ohms. The wiring of the potentiometer was changed to the modified form as shown. The glass electrode assembly, represented diagrammatically, contains a calomel half-cell attached to the main potentiometer. A salt bridge connects to a vessel which contains the standard buffer or the solution whose pH is to be measured. The inside of the glass membrane contains a quinhydrone half-cell which makes contact with a highly insulated tapping key. An accessory potentiometer containing switch S_6 supplies a variable voltage by means of a coarse (1000-ohm) and a fine (100-ohm) adjustment. A microammeter (zero center) with a suitable shunt can be thrown to three different positions, *Q*, *S*, and *G*, by double pole triple-throw switch S_5. The lower circuit is a voltage amplifier system using alternating current tubes for filament supply. It was found advisable to use a dry-cell B-battery supply for steadiest conditions. The resistors and condensers should be of good grade material (Shallcross resistors are used) and it is recommended that the 0.1-microfarad condenser in the grid circuit of the first tube be mica to eliminate absorbed charge.

The resistance values given are those for an older type of potentiometer. If another type of potentiometer is used, the shunt and series resistances can be calculated from the formulas

$$\text{Series resistance} = R(1 - K_T)$$

$$\text{Parallel resistance} = \frac{K_T}{1 - K_T} \cdot R$$

where R is the total resistance of coils and slide wire from which the variable voltage is obtained. K_T is the voltage per

unit pH and is a function of temperature. If a newer type of student potentiometer (Leeds & Northrup) is used, where R = 2300 ohms—that is, twenty-two 100-ohm coils plus 100-ohm slide wire—then the series and shunt resistances are as follows:

Temperature, ° C.	15	25	35	45
KT, volts	0.5713	0.5912	0.6110	0.6309
Series resistance, ohms	986.9	940.4	895.6	848.8
Parallel resistance, ohms	3065	3325	3613	3931

The slide wire and coils of the potentiometer, from which the known balancing voltage is obtained, are shunted by a variable resistance so that the potentiometer dial reads not voltage but pH. The 100-millivolt potential drop across each coil and slide wire in the main potentiometer, after introducing the shunt, is reduced to 57 to 61 millivolts, the exact shunt resistance and voltage drop depending on temperature. A simple calculation and calibration give the proper shunt resistance for each temperature used. In order to maintain the total circuit resistance the same after introducing the shunt, a variable series resistance is placed in series with the slide wire and decade coils. The series resistances for various temperatures can be computed. A single-pole double-throw switch, S_2, throws into the circuit the extra series and parallel variable resistors, thus changing the instrument by means of a single switch from a voltage potentiometer to a potentiometer reading in pH units. The setting of these two variable resistors is determined by temperature and is read from a table obtained by a preliminary calibration which, once made for a given instrument, remains fixed.

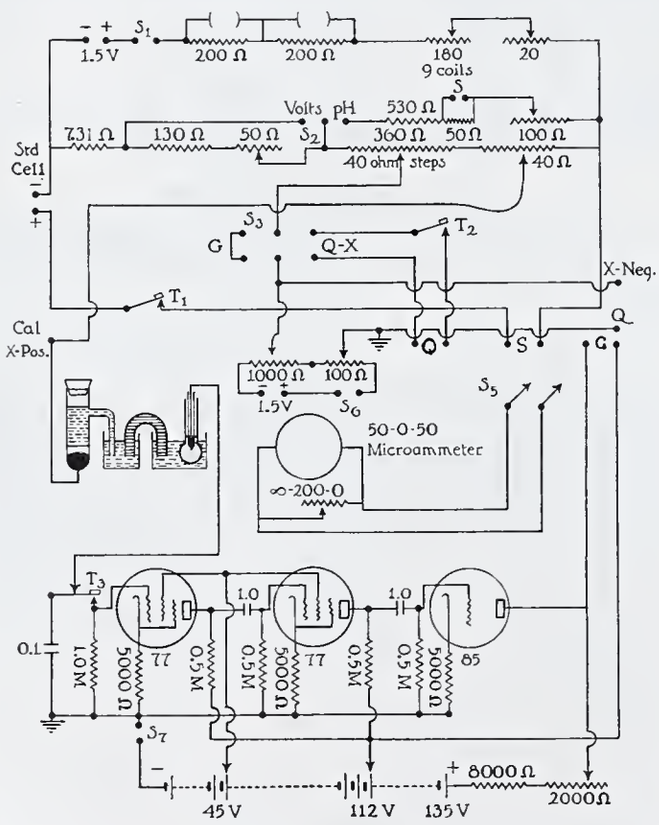

Figure 1. Diagram of Meter

An additional accessory potentiometer is placed in series with the glass-electrode system and the main potentiometer. It is interposed between the main potentiometer and the condenser to be charged. This potentiometer balances out the voltages, which for a given temperature are fixed and include the calomel half-cell voltage plus asymmetric potential of the glass membrane plus the quinhydrone voltage of the inner half-cell.

Operation of Meter

In an actual manipulation, switch S_1 is closed and the microammeter connected to S. Switch S_2 is thrown on "volts" and the preliminary standard cell balance is made by adjusting the main potentiometer circuit resistors and tapping key T_1 until a balance results. This is the usual procedure for any potentiometer. The filament heating circuit is closed (not shown on diagram), as well as the B-battery switch, S_7, and the accessory potentiometer switch, S_6. These are assembled as a single switch. The microammeter is thrown to position G. (It is advisable to shunt the microammeter with a low resistance while making this manipulation and it is important that the filament heating current be started before switching to G. The reason is that the microammeter in position G measures the difference between two opposing currents—namely, the plate current of the last tube and the balancing current from the last 22 volts of the B-batteries. If the filament is cold, there is a considerable unbalance due to the nonexistence of the plate current.) A buffer of known pH is placed in the container outside the glass membrane. The temperature is read and thereafter maintained constant.

The settings of the variable resistor in series and parallel with the main potentiometer slide wire and coils are made, the settings being obtained from the previous calibration. Switch S_2 is closed toward the side marked pH, and the main potentiometer dial is set on the pH of the standard buffer. Thus, if a standard acetate buffer pH = 4.63 is used, the main potentiometer scale is set on 0.400 (coil decade) + 0.063 (slide wire). The double pole switch, S_3, usually remains fixed in position G for glass-electrode work. The accessory potentiometer (containing switch S_6) is now adjusted, using both fine and coarse adjustments, while key T_3 is tapped until there is no ballistic throw on the microammeter with maximum sensitivity (shunt infinity). The accessory potentiometer then remains fixed. To measure the pH of any unknown solution, the unknown replaces the standard buffer and key T_3 is tapped while the main potentiometer is varied, the accessory potentiometer remaining fixed. When a balance is obtained, the main potentiometer reads the pH of the unknown. Any number of determinations may be made after this single preliminary calibration with standard cell and standard buffer, provided the battery voltages of the two potentiometers do not change.

The pH measurement is simple, involving only a preliminary standard cell and standard buffer adjustment with appropriate dial settings and operation of the proper switches. This instrument has been in operation for 3 months and has given excellent results. It has been operated by students and technicians with no knowledge of vacuum-tube technic. A simple pH measurement can be made in about 10 minutes, including the time required for the constancy of the filament and batteries. Once in adjustment, repeated measurements can be made in one minute.

No temperature calculation is necessary. This is taken into consideration by the variable calibrated resistors in parallel and in series with the slide wire and coils.

It is not necessary to know the value of the voltage of the calomel half-cell, the quinhydrone half-cell, nor the asymmetric potential. This remains constant for a given temperature and is balanced out by the accessory potentiometer. The main potentiometer balances the membrane potential, which varies directly with the pH.

In order to use the instrument for measuring quinhydrone and hydrogen-electrode potentials, switches and binding posts are provided (Figure 1).

The accuracy of the instrument is about 0.02 pH. The instrument is easily portable, the ammeter is inexpensive and of rugged construction, and the vacuum tubes are of standard type and inexpensive. Such an instrument will have its greatest range of usefulness in biological and industrial laboratories where rapid measurements are desirable by technicians not especially expert in vacuum-tube operation. Although the operation is simple, it is recommended that those un-

familiar with vacuum-tube circuits consult a radio engineer for minor details of construction before an attempt is made to build such an assembly. The approximate costs of the various parts are: amplifier resistors, $5; tubes, $4; paper condensers, $1; mica condenser, $5; condenser discharge key, $3; batteries, $4; filament transformer, $2; microammeter and shunt, $15; accessory potentiometer, $2; shunt and series resistors for main potentiometer (with dials), $4; student potentiometer, $70.

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Determination of Sulfur in Plain and Alloy Steels

A Perchloric Acid Modification of Meineke's Method

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THE time required for gravimetric determination of sulfur in steels by Meineke's method may be decreased by substituting perchloric acid evaporation for hydrochloric evaporation. The steel is dissolved in the potassium-copper chloride solution which leaves insoluble all the sulfur, carbon, some chromium, iron, molybdenum, etc. The residue may be taken up in acids, and fumed down with perchloric acid. The insoluble material is then separated from the soluble sulfates which are precipitated after reduction of chromates.

When running a batch of sulfurs the points which deserve consideration are: the substitution of paper for Gooch crucibles; a single evaporation with perchloric acid, instead of several with hydrochloric acid, to get rid of nitric acid; and a slight danger of spattering during evaporation of the acid.

The determination of sulfur after fuming a sample by perchloric acid has been applied for some time to sulfur in rubber, so that it is only a matter of application to steels. The steels under consideration were those containing molybdenum or selenium which give low results by the evolution method, and any high-sulfur steels which may tend to give low results by that method.

Procedure

Five grams of steel are transferred to a 600-cc. beaker or flask and covered with 500 cc. of the potassium-copper chloride solution. The solution is kept at about 90° C., as on a steam bath. Copper immediately comes out of the solution, and the reaction is complete when the bright red metal has redissolved. The solution is kept covered at all times, but agitated frequently to hasten solution if desired. With hand stirring, the time required is 2 or more hours.

The hot solution is filtered through a fast filter paper, and washed with hot water. The paper is removed from the funnel, placed in a beaker, covered with strong bromine water, and agitated with a glass rod. Now 10 cc. of zinc oxide–nitric acid, and 8 cc. of c. p. perchloric acid are added. The beaker is heated to destroy the paper and drive out the nitric acid and the excess perchloric acid. Upon completion of heating, as indicated by the formation of chromic acid (if chromium is present), or by the clarification of the fumes in the beaker, and condensation of perchloric acid on the sides of the beaker, the beaker is removed from the heat and cooled. As carbon does not interfere, heating need not be continued to oxidize it.

The residue, usually solid, is dissolved in water, diluted to about 100 to 150 cc., and boiled to remove chlorine. The silica (and carbon) is filtered off on paper and washed with water. To the filtrate are added 10 cc. of peroxide (to reduce chromic acid), the solution is diluted to 200 cc. and boiled, and sulfates are precipitated with barium chloride, as is customary. The weight of barium sulfate in grams divided by 5 and multiplied by 0.1373 gives the weight of sulfur found per gram.

This perchloric acid modification for the determination of sulfur checks Meineke's method.

To show that various reagents encountered in analysis of sulfur do not interfere. a series of four sets was run as follows:

1. 25 cc. of approximately 0.1 *N* sulfuric acid, run for sulfates.
2. 25 cc. of approximately 0.1 *N* acid plus 10 cc. of zinc oxide–nitric acid reagent and 8 cc. of perchloric acid.
3. 25 cc. of approximately 0.1 *N* acid plus 1 gram of potassium chlorate and 5 cc. each of nitric and hydrochloric acids and 8 cc. of perchloric acid.
4. As in 2, and in addition 0.0586 gram of potassium chromate (0.0200 gram of chromium), and peroxide.

Results (grams of sulfur): (1) 0.0403, 0.0402; (2) 0.0403, 0.0402; (3) 0.0403; (4) 0.0403, 0.0402.

Table I. Typical Analyses

	C	Mn	P	S	Si	Ni	Cr	Mo
	%	%	%	%	%	%	%	%
Author's laboratory	3.00	0.62	0.169	0.082	2.37	1.80	0.37	0.60
Outside laboratory	3.00	0.70	0.11	0.06	2.31	1.91	0.37	0.70
	3.10	0.56	0.085	[a]	2.35	1.82	0.35	0.60
	3.00	0.68	0.051	0.064	2.30	1.87	0.40	0.62
	...	0.43	0.021	[b]	0.34	..	13.14	..
	0.086	0.40	0.022	0.221	0.27	0.22	13.3	..
	0.11	0.37	0.014	[c]	0.30	..	13.1	0.55
	0.15	0.37	0.016	...	0.25	..	13.1	0.56

[a] Evolution, 0.034; gravimetric, 0.067, 0.068 (author); 0.071, 0.072 (R. C. Coburn).
[b] Evolution, 0.256; gravimetric, 0.348, 0.344.
[c] Gravimetric, 0.09, 0.08 (author); 0.089, 0.089 (R. C. Coburn). Meineke, 0.077 (author); 0.08, 0.09 (R. C. Coburn).

Analysis of a selenium steel by the gravimetric method gave 0.246 and 0.245, and by the evolution method 0.132 per cent. Another gave 0.256 and 0.112 per cent, respectively.

Bureau of Standards steels analyzed for sulfur gave the following results: No. 10d, 0.030; author, 0.026, 0.026; No. 22b, 0.041; author, 0.034, 0.034.

Solutions Used

The following reagents were used: 500 grams of $(KCl)_2.CuCl_2.2H_2O$; 100 cc. of hydrochloric acid; and 2000 cc. of water. The zinc oxide–nitric acid reagent was prepared by sifting 200 grams of zinc oxide into 1 liter of concentrated nitric acid.

Conclusion

A modified method for the Meineke gravimetric sulfur determination, suggested because of greater speed in operation, has been applied successfully to molybdenum, selenium, and high-sulfur steels.

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Filtration of Hot Solutions

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THE problem of filtering hot concentrated solutions in recrystallization processes is sometimes perplexing, for the solution in the funnel and the main part of the solution must be kept hot to prevent premature crystallization. The use of a jacketed funnel is common, but not too satisfactory when large quantities of rather slow-filtering solutions are being handled (*1*).

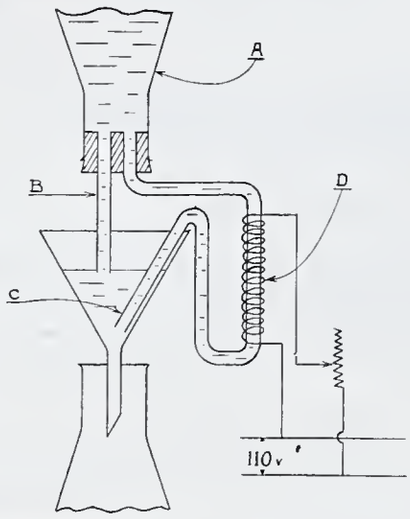

FIGURE 1. DIAGRAM OF APPARATUS

The device described here is of service in filtering large volumes and keeping the solution hot with a minimum of attention from the experimenter, and has been found satisfactory with water and benzene solutions. In one test experiment an asbestos filter was used with a strongly acid, concentrated solution of sodium hydrogen sulfate; this solution filtered very slowly, yet no difficulty was experienced in keeping the temperature (measured in the funnel) at 70° to 75° C. for the several hours required for the filtration. The device has the advantages that it heats not the funnel but the solution being filtered, and that it automatically keeps the funnel filled and therefore requires attention only at the start and at the finish of the filtration.

The design of this apparatus may be varied. The section at *D* may be inclined, and a free flame used as the source of heat if nonflammable solvents are used. The writer has used a jacketed tube with steam heat for benzene solutions, but the electric heating unit seems most satisfactory for all purposes.

Constant level is maintained in the funnel because air is not admitted to inverted flask *A* until the level in the funnel goes below the end of tube *B*. Working on the thermo-siphon principle, the coolest of the solution in the funnel is withdrawn through tube *C*, heated at *D*, and returned to *A*. When the level in the funnel falls below the end of *B*, air enters here, and the flow of the liquid through the heating coil is temporarily reversed. This does no harm. Care must be taken to see that the stopper in flask *A* is securely in place.

In constructing the heating unit, *D*, the glass tube is covered with thin asbestos paper, then wound with No. 26 chromel wire (resistance of heating coil about 10 ohms), and covered with asbestos insulation. It has been found that a current of about 2 to 4 amperes results in satisfactory heating.

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A Simple Laboratory Stirrer for Use on the Vacuum Line

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IN LABORATORY work with small quantities of organic chemicals, it is frequently necessary to stir for extended periods of time. For laboratories not having pressure lines, the vacuum stirrer shown above will be found very convenient. It is extremely inexpensive, requires little time to make, and is powerful. If carefully made it will stir viscous liquids, and is especially applicable for use in the synthesis of the Grignard reagent. For schools, it is very handy for students in second-semester organic work, where it is inadvisable and expensive to place electric motors in their hands.

The housing is a small can, such as is used to contain chocolate. The tin blades for the vanes are made from any sheet metal, and may be soldered together and fastened to the shaft with de Khotinsky cement, or any other available wax. The fitting between the shaft and the bearing should be tight to prevent leakage of air, and should be lubricated with light oil. The use of a nozzle on the air inlet increases the power greatly. A second air inlet will increase the power. A little variation in the size of the opening will lead to better results. The connection of the shaft to a longer one is accomplished by means of a rubber policeman. For use in potentiometric titration, or where a mercury seal is not required, the shaft may be an unbroken rod with the propeller sealed upon the end as shown in Figure 1.

RECEIVED March 12, 1935.

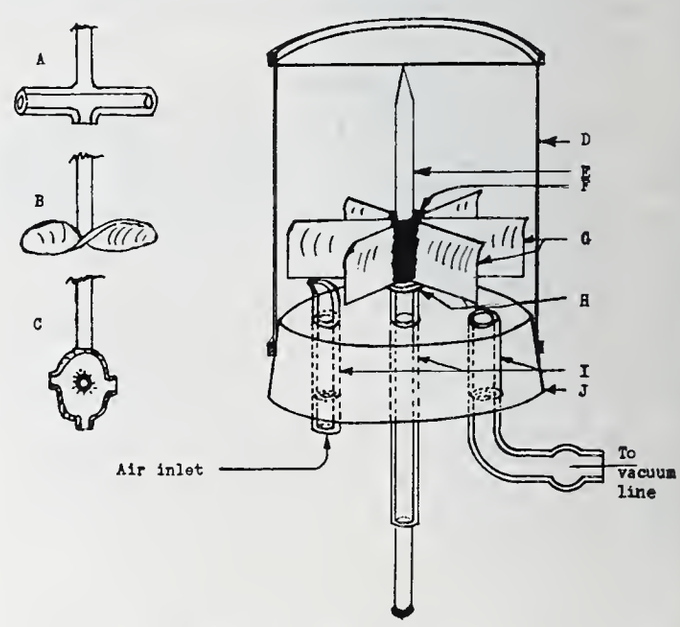

FIGURE 1. DIAGRAM OF STIRRER

A, B, C. Best types of agitators for use with this stirrer
D. Small tin can
E. 3-mm. glass rod
F. de Khotinsky cement
G. Sheet-steel vanes
H. Two small washers
I. 5-mm. tubing
J. No. 11 rubber stopper

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HARRISON E. HOWE, EDITOR

General Microchemistry

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MICROCHEMISTRY may be defined as the systematic presentation of the technic involved in the performance of chemical experiments on an essentially smaller scale than is usually employed in laboratory practice. In accordance with the atomic concept of matter, the chemical phenomena and physical properties observed on the smallest quantities of matter handled up to the present time in microchemical experiments (10^{-9} gram or approximately 10^{12} molecules) cannot be expected to differ essentially from those observed on a large bulk of material. (Phenomena belonging to the fields of colloid chemistry, the study of radioactive elements, etc., are not considered here.) It is obvious, however, that the technic of working and the methods of observation must vary with the amount of material under consideration.

Field of Microchemistry

General microchemistry (*3*) deals with the development, testing, correlation, and systematization of methods for the handling of small quantities of materials, and for the observation and determination of their properties. It has the task of supplying the working technic used in applied microchemistry, of which microanalysis represents up to the present time the most important branch. Certainly more than nine-tenths of the microchemical methods carried out are used in microanalytical procedures.

According to the definition, the upper limit for the size of material to be handled by microchemical methods is reasonably defined by stating that the quantity of material taken should be so small as to prohibit the use of traditional working methods. The lower limit is, of course, determined by the state of advance of microtechnic. It is obvious that both limits of the amount of material depend on the nature of the individual problem and will undergo changes in the course of time. If chemists should succeed, for example, in increasing the sensitivity of an analytical procedure by increasing the molecular weight of the precipitate to such an extent that 1-mg. samples could be analyzed by the standard methods of today, then the use of microtechnic as applied today to the analysis of 1-mg. samples would probably permit the analysis of 0.01-mg. samples. Such an advance would simply effect a shift of both limits of the range of microanalysis in favor of still smaller samples. The example also illustrates the relation between the sensitivity of tests and the necessity of using microchemical technic for their performance: the more sensitive the test, the smaller the quantity of material which may be analyzed without the use of a microchemical technic. The simultaneous use of sensitive tests and microchemical methods, however, promises the attainment of extremely low limit of identification.

The principal task of most chemical work (analytical as well as preparative) is the isolation of the components contained in a mixture, and their subsequent identification or estimation. The isolation itself usually comprises the preparation of suitable compounds, followed by their separation and purification. Identification and estimation are nearly always based upon the observation or measurement of physical properties—states of aggregation, transition temperatures, shape, density, mass, volume, color, refraction and reflection of light, radiation, magnetic susceptibility, etc.—which can be directly or indirectly recognized by sensory impressions. When the size of the specimen under investigation becomes very small, a refined manipulative technic must be employed, and the manifestations of the physical and chemical properties must be amplified by suitable devices in order to be registered by our sense organs. General microchemistry provides these special technics.

Micromethods must be rather closely correlated to the amount of material available, and the size of sample which may be taken for a microanalysis varies over a wide range. In general, approximately 10 to 50 mg. constitute the upper limit of sample size for qualitative and quantitative microanalysis. The smallest sample may at present be considered 0.1 microgram (0.1 gamma, 0.0001 mg.), since it is possible to collect and recognize quantities as small as 0.00003 γ of hydrogen ion, 0.0002 γ of hydroxyl ion, 0.0005 γ of borate ion, 0.0003 γ of cobalt or nickel ion, about 0.001 γ of antimony or silver ion, or about 0.01 γ of sulfide, arsenic, cadmium, copper, iron, lead, or mercury ion (*2*). Furthermore, it is possible to collect and measure such small quantities as 0.001 γ of gold (*5*) and 0.01 γ of mercury (*9*). As little as 0.00001 γ of thorianite should be sufficient to detect the helium occluded in such material (*7*), and only 0.005 γ of air is required for a quantitative analysis by the bubble method of Krogh (*6*). Gravimetric residue determinations with a few micrograms of sample have already been carried out in great numbers at Emich's institute (*10*), and the use of microbalances of extreme sensibilities—0.0002 γ and less—should make it possible to work with still smaller samples.

A variation in the size of a microsample from 0.1 γ to 50 mg. corresponds to a variation in the weight of a macrosample from 1 gram to 500 kg. Consequently, the manipu-

lative technic and methods of observation used in microanalysis must undergo vast changes as the amount of material decreases. These changes must be even more radical than those taking place when reducing the quantity of the sample from 500 kg. to 1 gram, as the corresponding range in microanalysis extends below the limit where the palpable properties of matter can be directly observed by the human sense organs. This fact, together with the observation that a reduction to one one-hundredth of the original mass manifests itself in a less obvious way when working on a small scale (compare the reduction of a mass from 10 to 0.1 mg. with the reduction from 100 to 1 kg.) necessitates a close correlation between mass and technic in microanalysis, a fact which is usually overlooked but which cannot be emphasized too much.

Microtechnic

The development of a system of microtechnic for chemical work was begun by Emich in 1900 and essentially completed by 1911, when the first edition of his Lehrbuch (*3*) appeared. This part of Emich's work has not only contributed toward the rapid progress of microchemistry in the last two decades, but was actually the foundation of microchemistry (*8*).

The technic of quantitative analysis and of preparative work, and the methods for the observation of properties (physico-chemical work) have been developed with proper consideration of adaptability to certain size ranges of matter. Emich must have recognized this requirement at a very early stage of his research, and he repeatedly emphasizes the importance of its strict observation.

When a sample of a few centigrams is taken for analysis (semi-microanalysis, or centigram method), the use of centrifuge tubes of 3- to 15-cc. capacity is recommended. In most cases it will be possible to effect the separation of solid and liquid phases by simply pouring out the filtrate after centrifuging. Filtration through paper could be used, but is less efficient. Spot tests are suggested as confirmatory tests.

With samples of 0.5 to 1 mg., small centrifuge tubes (microcones) of 0.7-cc. capacity are most efficient for the separation of solid and liquid phase. The use of a microscope is still not necessary, as the presence and color of precipitates 5 to 10 γ in weight, or of colorations caused by these amounts, can be observed with the unaided eye. Spot tests suggest themselves as confirmatory tests here; however, the certainty of identification is increased by the use of tests carried out with microscopic observation.

A complete scheme for the isolation, identification, and estimation of the commoner cations has been worked out, and will be presented soon in book form (*1*). The results, which may be obtained without difficulty, may be illustrated by the analysis of a 1-mg. "unknown" sample: Al, 3 per cent found (3 per cent given); Fe, 0.1 (none); Cr, 1 (1.5); Mn, 1 (1.5); Zn, 1.5 (1.5); Ni, 0.7 (1.5); Ca, 0.4 (1.5); PO_4, not estimated (1.5). The iron found was introduced by the rereagents used. If the purity of the reagents has not been tested, the detection of less than 2 γ of iron, calcium, or sodium, which constitute very common impurities of the "pure" reagents, should never be taken as proof of their presence in the sample.

A technic of working in capillaries of 0.5- to 1-mm. bore has been developed (*4*) for the analysis of 0.05- to 0.5-mg. samples (a centi-milligram procedure), whereby practically all the processes required in qualitative analysis can be carried out with ease and certainty. A magnifying lens, or a low-power microscope becomes a necessary tool for the detection of precipitates and colorations.

The use of laboratory apparatus of the ordinary type becomes absurd when the size of the sample decreases to a few micrograms or less, since the small quantities of precipitates or the tiny drops of solution cling to any surface. Continuous control of all operations by means of the microscope becomes imperative, magnifications of 50× to 100× being necessary for the observation of the confirmatory tests. Emich succeeded in handling such small quantities of matter by absorbing them on the ends of textile fibers. Precipitates, formed by dipping the fiber into droplets of reagent solutions, cling to the fibers and can be transferred without difficulty to other solutions which may serve for washing the precipitates, extracting parts of them, etc. At the same time, the material under investigation always remains concentrated in a very small area, thus preventing its loss and facilitating observation.

Microtechnic has already contributed greatly to the progress of science, but one cannot expect it to realize its full potentialities in that direction until the great majority of research men—not only the chemists but also biologists, geologists, archeologists, etc.—are informed as to the possibilities of microchemical work. Even Pregl would not have begun the development of organic quantitative microanalysis had it not been for the knowledge of the previous work of Emich which indicated the feasibility of the proposed task (*8*).

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Etching Stainless Steels. A new method for etching stainless steel, prior to microscopic study of grain structure, has been developed in the National Bureau of Standards.

All metals are composed of small, imperfect crystals known as grains, the size, shape, and structure of which are of great importance in the study of any metal and its application in service. To reveal this grain structure it is necessary to etch the metal with a chemical reagent. The appearance is then studied under the metallurgical microscope at suitable magnifications.

Certain metals are difficult to etch satisfactorily because of their compositions. Stainless steels are among the most troublesome, since they resist all ordinary reagents. In the past it has been necessary to use strong, mixed acids to reveal the structures of stainless steels, and these mixtures require great care in handling and in disposing of them afterwards.

The new method was worked out in connection with a study of the changes induced in stainless steels by welding. The stainless steel is etched electrolytically in oxalic acid (10 grams dissolved in 100 milliliters of water), the specimen being the anode and a piece of platinum the cathode. Current is supplied from four dry cells in series or from a 6-volt storage battery. The carbides are revealed in from 15 to 30 seconds' etching time, while an additional 30 to 45 seconds will reveal also the grain boundaries of the "18–8" (18 per cent chromium, 8 per cent nickel) type of stainless steel. The solution is relatively rapid in etching action and does not stain the specimen.

Catalytic and Induced Reactions in Microchemistry

I. M. KOLTHOFF AND R. S. LIVINGSTON, University of Minnesota, Minneapolis, Minn.

The general theory of catalysis and induction in homogeneous systems is discussed. Induced and catalyzed precipitations are mentioned briefly, followed by a general discussion of analytical applications. Finally, the catalytic and inducing effects of silver and mercury and some new tests are described.

ALTHOUGH catalytic and induced reactions are widely used in the detection and quantitative estimation of certain ions or compounds, not much theoretical work has been done on the mechanism of most of these reactions. It is rather deplorable that most of our knowledge in this field is empirical. If the theory underlying catalytic and induced reactions were known more explicitly, it might be expected that a systematic application of the theoretical fundamentals would result in the discovery of many useful reactions for the qualitative detection and quantitative estimation of microquantities of substances.

Homogeneous catalysis of oxidation-reduction reactions occurs when the catalyst can exist in an oxidized and a reduced form and when these forms of the catalyst are capable of reacting rapidly with the reducing and oxidizing agents, respectively. A simple and well-known example of this type of reaction is the catalysis by the iodine-iodide couple of the oxidation of thiosulfate ion by hydrogen peroxide in slightly acid solution. The kinetics and stoichiometry of this reaction may be summarized by the following chemical equations:

$$H_2O_2 + I^- \rightarrow IO^- + H_2O \qquad \text{(1, rate determining)}$$
$$IO^- + H^+ \rightleftarrows HIO \qquad \text{(2, rapid, reversible)}$$
$$HIO + I^- + H^+ \rightleftarrows I_2 + H_2O \qquad \text{(3, rapid, reversible)}$$
$$I_2 + I^- \rightleftarrows I_3^- \qquad \text{(4, rapid, reversible)}$$
$$I_3^- + 2S_2O_3^= \rightarrow \rightarrow S_4O_6^= + 3I^- \qquad \text{(5, rapid, probably complex)}$$
$$H_2O_2 + 2S_2O_3^= + 2H^+ = S_4O_6^= + 2H_2O \qquad \text{(6, stoichiometric)}$$

Equation 6, which represents the stoichiometric reaction, is the sum of the five preceding equations which represent the reaction steps. Although the specific reaction rate of reaction step 1 is very much smaller than that of reaction step 5, the steady-state concentration of I_3^- is under ordinary conditions so small that the absolute rates of reactions 1 and 5 are equal. Any one of a number of similar processes would serve equally well to illustrate this type of catalysis. Typical examples are the decomposition of hydrogen peroxide catalyzed by the iodine-iodide (*1*), the bromine-bromide (*5*), or the chlorine-chloride (*22*) couples, and the oxidation of chromic to dichromate ion or of ammonium ion to nitrogen (*24*) by peroxysulfate ion catalyzed by the trivalent-monovalent silver couple. Acid-base catalysis has not been mentioned in the foregoing discussion, only because it was felt that a discussion of this phenomenon would not contribute anything useful to the study of catalysis in analytical chemistry. Of course (generalized) acid-base catalysis as well as kinetic salt and solvent effects (*7*) play important roles in determining the rate of oxidation-reduction reactions.

Efficient catalysts for a given reaction can be selected (without direct trial) whenever the rates of the reaction steps are known. For example, in the case just cited it is well known that the rate of oxidation of thiosulfate ion by iodine is extremely rapid and that hydrogen peroxide oxidizes iodide ion more rapidly than it oxidizes thiosulfate ion. On the basis of this evidence, we could predict with certainty that the iodine-iodide couple would act as an efficient catalyst for the oxidation of thiosulfate by hydrogen peroxide. On the other hand, we could predict that the chlorine-chloride pair would not be an efficient catalyst for this reaction, since the rate of oxidation of chloride ion by hydrogen peroxide is known to be slow. Unfortunately, such information about the rates of the reaction steps involved is commonly not available and a consideration of the free energies of the probable reaction steps is the only systematic guide which we can use in selecting catalysts. While this method does not enable one to predict that any possible catalytic pair will be an efficient catalyst for a given reaction, it does greatly simplify the problem by excluding many substances which might otherwise be considered as possible catalysts.

As an example of this method, let us consider the oxidation of arsenious acid by ceric ion in an acid solution. Since the free energy of a reaction is the algebraic sum of the free energies of its constituent half-cell reactions, the free energy data may be conveniently summarized by plotting the half-cell potentials (*4*) of reactants and possible catalysts against pH (Figure 1). It should be emphasized that this plot is not intended to imply that any electrochemical mechanism of catalysis exists, it is merely a convenient method of representing free energy or equilibrium data. In preparing the plot no attempt has been made to allow for secondary effects of pH—i. e., the electromotive force of the Ce^{++++}, Ce^{+++}

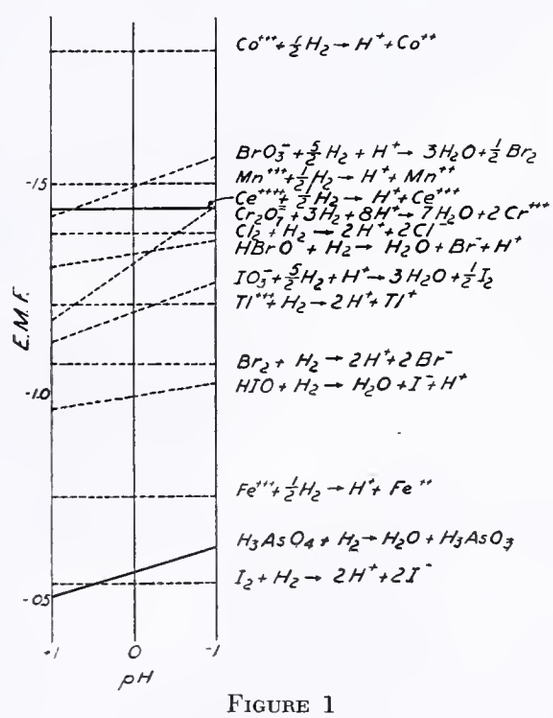

FIGURE 1

half-cell at pH = 1 is not the e. m. f. which would be obtained in a half-cell prepared with equal amounts of cerous and ceric salts dissolved in 0.1 *N* acid, but is the potential which the half-cell would have if the activities of the ceric and cerous ions were equal.

When the half-cell potential of the catalytic pair lies between the half-cell potentials of the compounds taking part in the main (stoichiometric) reaction, the free energy of each of the two compensating catalytic reaction steps—steps 2 and 5 in the first case considered—will be negative, and the pair in question is a possible catalyst. All oxidation-reduction couples which do not satisfy this condition cannot act as catalysts for the given reactions. For the ceric arsenite reaction a number of catalytic couples satisfy this condition. Of these, only compounds of iodine (*17*) and bromine are found to catalyze the reaction measurably, and the effect of bromine is too small to be of any practical value. The diagram indicates that the iodine-iodide pair will probably not be effective, but that either the hypoiodous-iodide or the iodate-iodine couple should be capable of acting as an efficient catalyst. It is very probable that the hypoiodous-iodide pair is the active catalyst, since it is well established that hypoiodous acid is intermediate in the oxidation of arsenite by triiodide ion. While the diagram does include as possibilities a number of compounds which are not efficient catalysts, it definitely excludes such, otherwise probable, couples as the manganic-manganous and cobaltic-cobaltous. The method is of greater practical value when the free energy of the main reaction has a smaller (negative) value—i. e., when the potentials of the corresponding half-cells are not so widely separated.

Induced Reactions

In some cases the rate of an oxidation-reduction reaction is greatly increased when one of the reactants is simultaneously oxidizing or reducing some other substance. Such reactions are called induced or coupled reactions. The simultaneous oxidation of manganous ion and arsenious acid by chromate ion,

$$CrO_4^{=} + H_3ASO_3 + Mn^{++} + 6H^+ = H_3AsO_4 + Mn^{+++} + Cr^{+++} + 3H_2O$$

is an example of a simple induced reaction. In the absence of arsenious acid the oxidation of manganous ion by chromate ion is extremely slow. But in the presence of arsenious oxide, and under favorable conditions, one mole (1 equivalent) of manganous ion is oxidized for each mole (2 equivalents) of arsenious acid oxidized. This corresponds to a maximum induction factor—i. e., the ratio of the equivalents of the induced oxidation to the equivalents of the primary oxidation—of one-half. A possible, although by no means established mechanism of this process may be represented by the following equations:

$$CrO_4^{=} + H_3AsO_3 \rightarrow H_3AsO_4 + CrO_3^{=} \quad \text{(7, relatively rapid)}$$
$$2CrO_3^{=} + H_3AsO_3 + 10H^+ \rightarrow \rightarrow H_3AsO_4 + 2Cr^{+++} + 5H_2O \quad \text{(8, slow, probably complex)}$$
$$CrO_3^{=} + Mn^{++} + 6H^+ \rightarrow \rightarrow Mn^{+++} + Cr^{+++} + 3H_2O \quad \text{(9, rapid, probably complex)}$$

The sum of Equation 8 and twice Equation 7 gives the stoichiometric equation for the primary reaction.

$$2CrO_4^{=} + 3H_3AsO_3 + 10H^+ = 3H_3AsO_4 + 2Cr^{+++} + 5H_2O \quad \text{(10, stoichiometric)}$$

When the reaction step represented by Equation 9 occurs very much more rapidly than that represented by Equation 8, an induction factor of 0.50 is realized and the total stoichiometric reaction is represented by Equation 11.

$$CrO_4^{=} + H_3AsO_3 + Mn^{++} + 6H^+ = H_3AsO_4 + Mn^{+++} + Cr^{+++} + 3H_2O \quad \text{(11, stoichiometric)}$$

In many of the practically important examples of this type of reaction, the oxidation of a reducing agent by atmospheric oxygen is greatly accelerated by its simultaneous oxidation by some oxidizing reagents. The oxidation of stannous chloride by dichromate in the presence of air is a well-known example of this type of induced reaction. The value of the induction factor increases as the ratio of the concentration of dissolved oxygen to the concentration of the primary oxidant is increased. In practice this ratio depends on such factors as order of mixing, rate of stirring, etc. In some cases the induction factor is also a function of the concentration of hydrogen ion and even of the concentration of the reducing agent. If a proper choice of conditions results in a value of the induction factor much greater than unity, the induced reaction is said to be an example of "induced catalysis" (*6*). If on the other hand the induction factor cannot be made to exceed unity (or some other small number), the reaction is considered to be an example of "simple coupling." For all practical purposes, reactions of the "induced catalysis" type are of greater importance.

A possible mechanism for reactions of this type is catalysis (of the reduction of oxygen) due to a catalytic couple, one member of which is an intermediate in the primary reaction. When the oxidation by oxygen is a chain reaction, "induced catalysis" may be the result of the starting of reaction chains by an intermediate of the primary reaction. This latter mechanism has been clearly demonstrated for such reactions as the atmospheric oxidation of sulfite, induced by its primary oxidation with hydrogen peroxide. For this special class, the induction factor will be greatly decreased by the presence of a suitable inhibitor (*3*). In some cases even microquantities of an inhibitor produce a marked decrease in the reaction rate. This suggests that the inhibiting effect of a substance could be used to determine its concentration michrochemically. Unfortunately, the inhibiting effect is seldom very specific, which greatly reduces the general utility of the method. However, it might be used to determine the concentration of an inhibitor in a solution which was known to be free of all substances which could act either as an inhibitor or as an inducing agent for the reaction.

Induced and Catalyzed Precipitations

The theory underlying induced and catalyzed precipitations is different from induced and catalyzed reactions in homogeneous systems. Two different cases may be distinguished:

1. A constituent forms a slightly soluble crystalline compound upon addition of a suitable reagent. If the constituent is present in extremely small quantities (microconstituent) no precipitate is noticed, either because the amount is too small to be visible or because of super- or undersaturation. If in such a case a larger amount of another constituent (macroconstituent) is added, forming a slightly soluble compound with the same reagent, the microconstituent may be co-precipitated. Especially if the micro- and macrocomponents form mixed crystals, the enrichment of the microcomponent in the precipitate may be very pronounced. Thus a very dilute solution of lead does not yield a precipitate upon addition of sulfuric acid. If barium is added to the lead solution, mixed crystals of barium and lead sulfate are precipitated, the latter containing all the lead originally present in the solution.

Direct application of such "induced" precipitations to microdetection can be made when the microcomponent gives a colored precipitate with the reagent whereas the macrocomponent which is added yields a colorless precipitate. For example, nickel mercuric thiocyanate, which has a green-yellowish color, is precipitated by an alkali mercuric thiocyanate solution from relatively concentrated solutions

only. However, when zinc is added to the solution the white crystals of zinc mercuric thiocyanate are colored green if nickel is present. Korenman (*18*) makes use of the same principle for the detection of cobalt. In the presence of small amounts of cobalt the zinc mercuric thiocyanate has a blue color. Montequi (*25*) found that copper mercuric thiocyanate, which normally has a green color, yields a violet precipitate when precipitated together with zinc. The reaction is applied as a sensitive method for the detection of copper.

2. Heterogeneous Catalysis. It is beyond the scope of this paper to discuss the theory of heterogeneous catalysis. This has many analytical applications but the exact mechanism involved in most of these reactions has not been investigated yet. Upon treatment of various metal solutions with suitable reducing agents no metal is separated, although the reducing action of the agent is great enough to cause reduction to the metallic state. An alkaline stannite solution reduces the bismuth salts to metallic bismuth (*27*). Use of this reaction is made in the sensitive detection of bismuth. Lead salts are slowly reduced by alkaline stannite, this reduction being strongly accelerated by traces of bismuth. By adding some lead salt to the solution the reaction for bismuth with alkaline stannite solution can be made 250 times more sensitive (*13*). Various examples of induced reductions involving the formation of precipitates are given by Feigl (*8*). The catalytic effect of mercury in the reduction of arsenic by stannous chloride or hypophosphite reagent is mentioned in the practical part of this paper.

Analytical Applications

A substance is transformed into a reaction product which is readily detected. If the speed of transformation is slow, a suitable catalyst is added. Thus manganese is oxidized to permanganate by potassium persulfate in the presence of silver as a catalyst.

More general use is made of the catalytic and inducing properties of substances, for the qualitative detection and quantitative estimation of the catalyst.

Care should be observed in the interpretation of the results. Neither a positive nor a negative result as a rule is entirely conclusive regarding the presence or absence of a certain constituent (catalyst), for the following reasons:

1. The specificity of the catalytic or inducing action of the substance to be determined or detected must be considered. From the considerations presented in the theoretical part of this paper it may be inferred that in oxidation-reduction reactions various oxidizing or reducing substances, whose half-cell potential is intermediate between those of the two slowly reacting systems, may exert a catalytic effect. In many cases these changes in free energy are not known exactly. Therefore, after it has been found that a particular substance exerts a catalytic effect, a great number of substances (which might possibly serve as catalysts) should be tested also, in order to find how specific the catalytic effect is. Even if it has been found in an empirical way that the catalytic effect is quite specific for a certain reaction, it is not permissible to conclude the presence of this particular catalyst if a positive catalytic effect has been observed. The necessity for cautious interpretation may be inferred from the following example: It is mentioned by Feigl that traces of silver ion catalyze the reduction of tri- and tetravalent manganese in a hydrochloric acid solution. In testing the specific character of this test for silver the authors found that palladium exerts a similar effect, the reaction being even more sensitive for palladium than for silver.

2. The generality of the catalytic or inducing action must be considered. After it has been found that a substance exerts a catalytic effect, the question arises as to whether general use of this effect can be made for the detection and determination of the catalyst. It should not be overlooked that other substances present may make the catalyst ineffective. For example, silver and manganese can be detected by making use of the catalytic effect of silver upon the oxidation of manganese to permanganate by potassium persulfate in strongly acid medium. Halide ions interfere, because they either precipitate the silver or reduce the permanganate formed. In a study of the catalytic effect of silver the authors found that in the presence of an excess of solid magnesium oxide manganese is oxidized to permanganate on boiling with persulfate in the presence of silver as a catalyst. This effect is quite specific for silver, and traces of this element can be detected in this way (see below). However, in testing the limitations of this test for silver it was found that cobalt and chloride make the silver ineffective. In certain cases where two or more substances exert a similar catalytic effect it should be possible to make advantageous use of the masking effect, in order to make the reaction more specific. For example, it was found that traces of iodine (or iodide, or iodate) and of osmium exert a tremendous catalytic effect upon the reaction between ceric sulfate and arsenic trioxide in acid medium. In this case the iodide can be made ineffective by the addition of a small amount of mercuric mercury.

In the quantitative estimation of a catalyst use is made of the relation between the concentration of the catalyst and the rate of the catalyzed reaction. It should be realized that quite generally indifferent electrolytes affect the rate of a reaction. Therefore, this relation between concentration of catalyst and reaction rate should be known for the particular mixture in which the catalyst is to be determined. The difficulty as a rule can be eliminated in a practical way. The rate of reaction is determined first by mixing a measured volume of the solution in which the catalyst is to be determined with a measured volume of the reacting components. After the approximate amount of the catalyst is determined, about an equal but exactly known amount is added to the same volume of the solution originally taken, without changing the volume appreciably (additions with microburet or micropipet) and the measurement is repeated. If the rate of reaction is proportional to the concentration of the catalyst, the amount of the catalyst is readily calculated from the two sets of measurements. Various modifications of this procedure are possible. The simplest procedures for measuring the rate of reaction are found in those cases in which one of the reacting components is colored. The time required for obtaining a colorless solution is measured. A reversal of this procedure is possible if a color develops after one of the reacting components has been quantitatively oxidized or reduced. In other cases the amount of reaction product formed is measured quantitatively. The catalytic effect of copper in the oxidation of cysteine to cystine and the subsequent measurement of the oxygen evolved in a given time was used by Warburg (*28*) for the determination of microquantities of copper in blood and was applied to milk by Zondek and Bondmann (*29*). Great care, however, should be observed, since relatively large and variable readings are obtained in blanks (*2*).

Practical Applications

Since the catalytic or inducing effect is often exerted by extremely small traces of a substance, it is possible to make use of the catalysts for the microdetection and estimation of the particular substance. It is beyond the scope of this paper to give an exhaustive treatment of all catalytic and induced reactions which find application in qualitative and quantitative microanalysis. As examples, the catalytic and inducing effects of silver and mercuric mercury are discussed below and some new reactions are described.

Catalysis by Silver

1. The catalytic effect of silver ions in oxidation reactions is to be attributed to the intermediate formation of a higher oxidation state, probably of trivalent silver ions. The latter have a high oxidation potential and are not stable as such in aqueous medium. The catalytic effect of silver ions in the oxidation of manganese to permanganate, of trivalent chromium to chromate, and of trivalent cerium to ceric cerium in strongly acid medium by persulfate has been known for a long time. Use of it was made by Marshall (*23*) in the detection of traces of manganese. To the authors' knowledge the reaction has never been used for the detection of silver, although it was found to be highly sensitive.

Procedure. One milliliter of a manganous sulfate solution containing 0.1 mg. of manganese is diluted to 5 ml. with 4 *N* sulfuric acid and 1 ml. of the solution to be tested for silver is added. About 0.2 to 0.4 gram of potassium persulfate is then added and the tube is placed in a boiling water bath. In the absence of silver the solution remains colorless, even after 5 minutes of heating. In the presence of 0.05 γ (= 0.00005 mg.) of silver a distinct violet color appeared after 2 minutes of heating. The test is therefore sensitive to one part of silver in 20,000,000 parts of solution when 1 ml. of the unknown is tested in the above way.

The reaction is specific for silver. Osmium tetroxide, auric gold, palladium, cobalt, copper, mercury, and various other cations did not catalyze the reaction.

Halide ions interfere. Even traces of chloride in the solution prevent the formation of permanganate or make the reaction for silver much less sensitive.

It was found in this work that silver not only catalyzes oxidations with persulfate in strongly acid medium, but also in weakly acid and in alkaline medium. Thus manganese is oxidized to permanganate in sodium hydroxide, or sodium carbonate medium or in the presence of excess magnesium oxide. Silver also catalyzes the oxidation of lead to lead peroxide by persulfate in neutral or alkaline medium. Five milliliters of 0.1 per cent lead nitrate solution were treated with 5 ml. of 1 *N* sodium acetate and divided into two parts. One drop of 0.1 per cent silver nitrate was added to one part and 0.5 gram of potassium persulfate to both. The tubes were placed in a boiling water bath. A reddish brown colloidal precipitate of lead peroxide was formed in the presence of silver, whereas the blank remained clear, except for a slight white precipitate on cooling. This test for lead is not very sensitive and of little analytical significance, since many ions interfere with the silver catalysis. On the other hand the oxidation of manganese to permanganate in alkaline medium in the presence of silver as a catalyst is of analytical significance.

Detection of Manganese in Weakly Alkaline Medium. Fifty milligrams of magnesium oxide (manganese-free), 1 drop of 0.1 per cent silver nitrate, and 0.2 to 0.3 gram of potassium persulfate are added to 10 ml. of the solution to be tested for manganese. The tube is placed in a boiling water bath for 3 to 4 minutes, then removed and allowed to settle. A red-violet coloration in the supernatant liquid shows the presence of manganese. Sensitivity: 0.3 mg. manganese per liter gave a distinct pink color. It should be mentioned that the magnesium oxide should be tested in the same way for manganese. It was found that c. p. products of magnesium oxide contained traces of manganese. With large amounts of manganese (100 mg. per liter) a heavy precipitate of manganese dioxide is formed which masks the silver catalysis. The solution to be tested should not contain more than 10 mg. of manganese per liter. The reaction is specific for manganese, although cobalt and nickel interfere, giving black precipitates. The presence of 0.05 mg. of nickel did not affect the sensitivity of the reaction, but the same amount of cobalt decreased the sensitivity markedly. Chlorides interfere. By working in strongly alkaline medium the interference by chlorides is eliminated.

Detection of Manganese in Strongly Alkaline Medium in Presence of Chloride. To 10 ml. of solution are added 1 drop of 0.1 per cent silver nitrate, 0.5 to 1 ml. of 4 *N* sodium hydroxide, and 0.2 to 0.4 gram of potassium persulfate. The mixture is heated to boiling for 30 seconds to 1 minute and allowed to settle. A pink coloration of the supernatant liquid indicates the presence of manganese. The test is sensitive to 5 γ of manganese, corresponding to 0.5 mg. of manganese per liter. Cobalt interferes, but small amounts of nickel and copper may be present.

Detection of Silver in Weakly Alkaline Medium. To 10 ml. of the solution to be tested are added 1 ml. of a manganese chloride solution containing 100 mg. of manganese per liter, 50 mg. of magnesium oxide, and 0.2 to 0.3 gram of potassium persulfate. The tube is heated in a boiling water bath for 3 to 4 minutes, removed, and allowed to settle. A red-violet color indicates the presence of silver. The test is sensitive to 3 γ of silver in 10 ml., corresponding to a concentration of 0.3 mg. of silver per liter.

The reaction is specific for silver. Nickel, cobalt, and chloride interfere. In strongly alkaline medium chloride does not interfere, but the reaction becomes slightly less sensitive.

Detection of Silver in Strongly Alkaline Medium in Presence of Chloride. To 10 ml. of the solution are added 0.2 ml. of manganous sulfate solution containing 0.1 gram of manganese per liter, 1 ml. of 4 *N* sodium hydroxide, and 0.2 to 0.4 gram of potassium persulfate. The mixture is boiled for 30 seconds to 1 minute and allowed to cool. A blank without silver is used for comparison. A pink coloration shows the presence of silver. The test is sensitive to 5 γ of silver, corresponding to 0.5 mg. of silver per liter.

Copper catalyzes the oxidation, but the reaction is not sensitive for copper.

Palladium inhibits the silver catalysis; gold has a similar effect but not as pronounced as palladium. Cobalt interferes, but small amounts of nickel may be present.

2. Silver chloride is more or less soluble in stronger chloride solutions with the formation of a complex $AgCl_2^-$ ion. It was found by Lang (*20*) that brown solutions of manganic manganese (Mn^{III} and Mn^{IV}) are fairly stable in 2.5 *N* hydrochloric acid. Addition of a trace of silver catalyzes the reaction between the higher-valent manganese and chloride and the solution becomes colorless within a short time. Feigl and Fränkel (*12*) found that silver also catalyzes the reaction between ceric cerium and hydrochloric acid. In using a suitable manganic chloride solution in 2.5 *N* hydrochloric acid as a reagent they could detect on a spot plate 0.4 γ of silver (1 drop of a solution containing 8 mg. of silver per liter). The authors found a sensitivity of 1 γ silver, but in testing the specific character of the reaction noticed that palladium has a stronger catalytic effect than silver. In a spot plate 0.2 γ of palladium can be detected. With a suitable mixture of ceric nitrate and hydrochloric acid Feigl and Fränkel could detect 0.05 γ of silver. However, the authors found that the sensitivity was less than 1 γ. In addition it was found that palladium behaves like silver; the test, therefore, is not specific. Thallous thallium interfered badly with the test, a yellow precipitate and a rapid decoloration being obtained.

3. Silver salts exert an inducing effect upon the reduction of mercuric chloride by phenylhydrazine (*10*). In the absence of silver the mercuric chloride is reduced to calomel and then slowly to metallic mercury. In the presence of silver the black mercury separates instantaneously. Hahn (*14*) found that traces of silver accelerate reduction of mercuric chloride to calomel by hypophosphite in a well-buffered solution and makes use of this fact in a sensitive detection of silver.

Catalysis by Mercury

1. King and Brown (*16*) found that mercuric mercury strongly catalyzes the reduction of arsenite or arsenate in hydrochloric acid medium to brown arsenic by stannous chloride. The addition of enough mercuric chloride to make its concentration 0.00001 *M* before the addition of stannous chloride, hastens the appearance of the coloration, increases the sensitivity of Bettendorf's test 10- to 100-fold and enables the test to be made in a lower concentration of hydrochloric acid. The authors were able to confirm the catalytic effect of mercury upon the speed of reduction of the arsenic, but

did not find the extreme sensitivity mentioned by King and Brown.

Thus, 0.2 ml. of 10^{-3} *N* arsenic trioxide was mixed with 9 ml. of concentrated hydrochloric acid and 1 ml. of 1 *M* stannous chloride (in 6 *N* hydrochloric acid). Without addition of mercuric chloride, a slight coloration was visible after 15 minutes of standing. If 1 ml. of 10^{-4} *M* mercuric chloride was added before the stannous chloride, a faint color was perceptible after 2 minutes of standing. With 0.03 ml. of 10^{-3} *N* arsenite acid, stannous chloride, and mercuric chloride a doubtful coloration was perceptible after 15 minutes of standing (limit of sensitivity); without mercuric chloride no change was noticeable after the same time.

King and Brown mention that use of the catalytic effect of the mercury can be made in its quantitative approximation. This was confirmed by the authors of this paper. As an illustration the following experiments are given:

One-half milliliter 10^{-3} *N* arsenic trioxide, and x ml. of 10^{-4} *M* mercuric chloride were diluted to 9 ml. with concentrated hydrochloric acid, and 1 ml. *M* stannous chloride was added. As compared with a solution containing no mercuric chloride ($x = 0$), a distinct difference was noted after 2 minutes with 0.2 ml., 3 minutes with 0.1 ml., 5 minutes with 0.03 ml., 7 to 8 minutes with 0.1 ml. Silver and copper do not interfere. Palladium interferes badly with the arsenic and mercury test, since it gives a dark turbidity upon addition of stannous chloride (palladium metal). Gold also interferes.

The authors found that mercuric mercury also catalyzes the reduction of arsenic by hypophosphite.

Reagent 1, 10 per cent calcium hypophosphite in 25 per cent hydrochloric acid.

Reagent 2, reagent 1 freshly saturated with mercurous chloride.

Procedure. Three milliliters of the solution to be tested are mixed with 2 ml. of concentrated hydrochloric acid and 3 ml. of reagent, and placed in a boiling water bath.

Table I. Reduction of Arsenic by Hypophosphite

Arsenic Present in 3 Ml.	Time Required to Give Brown Turbidity	
γ	Reagent 1	Reagent 2
	Min.	*Min.*
300	1.5	<1
100	2	1
30	4	1
10	30 (doubtful)	1
5	..	4 (very faint)

Silver has no catalytic effect. The reagent saturated with mercurous chloride after a day of standing behaves as the mercury-free reagent, a deposit of calomel and mercury being found on the bottom of the bottle. Hence, if use is made of the catalytic effect of mercury in the detection of arsenic with hypophosphate reagent, it is advisable to add a suitable amount of mercuric chloride to the reacting mixture.

Feigl (*9*) found that mercuric mercury catalyzes the reduction of stannic tin to the stannous state by hypophosphite in hydrochloric acid medium. The stannous tin is detected by the addition of cacotheline with which it yields a characteristic amethyst color (*21*). This reaction, however, is not specific for stannous tin. Apparently, the cacotheline acts as an oxidation-reduction indicator, being reduced from the yellow to the violet form at relatively low oxidation potentials (*26*). In the authors' work it was found that the reduction of the stannic tin also occurs slowly in the absence of mercury. Therefore in applying the following procedure it is advisable to use a blank without mercury for comparison.

Reagents. Saturated solution of cacotheline in water, 0.1 per cent stannic chloride solution in 1 *N* hydrochloric acid, and 10 per cent solution of calcium hypophosphite in 25 per cent hydrochloric acid.

Procedure. To 1 ml. of the solution to be tested are added 2.5 ml. of stannic chloride solution, 1 ml. of calcium hypophosphite solution, and one drop of cacotheline. At the same time a blank is prepared using 1 ml. of water instead of the solution to be tested. Both tubes are placed in a boiling water bath for 20 to 30 seconds (not longer, or else the blank becomes colored too strongly). An amethyst to red color indicates the presence of mercury.

The test is sensitive to 0.5 gram of mercury, corresponding to 0.5 mg. of Hg^{++} per liter in 1 ml. of the original solution.

The reaction is not specific for mercury. Palladium catalyzes the reaction in the same way as mercury. Cupric copper gives the same test, even in the absence of stannic tin. Apparently the cuprous copper formed reduces the indicator.

Silver and especially osmium tetroxide inhibit the catalysis by mercury. Gold interferes, since it is reduced to the metallic state and gives a red colloidal solution.

In the above the authors have discussed catalysis by silver and mercury only. It is evident that great care must be observed in the analytical application of such catalyzed reactions. If a positive result is obtained, it is always necessary to apply confirmatory tests showing the presence of the catalyst, since there is no certainty that the catalytic test is specific. On the other hand, a negative result does not necessarily indicate the absence of the catalyst, since other substances present may inhibit or prevent the catalysis. Naturally the catalytic reactions may become more decisive after group separations have been made and after it has been shown that other constituents belonging to the same group do not exert a similar catalytic effect and do not interfere. In the quantitative application of catalytic reactions the same precautions should be observed.

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Recent Advances in Applied Microchemistry

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An attempt is made to illustrate by brief descriptions and literature citations the latest micromethods of qualitative and quantitative analysis, both inorganic and organic. The latest developments in the microtechnic of isolation and purification are discussed, together with the micromethods for the determination of the purity of compounds with special consideration of Emich's *schlieren* method.

APPLIED microchemistry, or better, the application of microtechnic to chemistry, may be subdivided into the following branches: qualitative and quantitative analysis, and methods of isolation and purification.

Qualitative Microanalysis

INORGANIC. Qualitative microanalysis involves the application of microtechnic to qualitative chemical problems, with or without the use of the microscope. While chemical microscopy centers in the use of the microscope, in qualitative microanalysis this instrument is merely used as an additional valuable tool. Qualitative microanalysis employs microprocedures of great variety, such as separations, filtration, distillation, sublimation, catalysis (*63*, *85*), electrolysis (*23*), fluorescence analysis (*64*), spot analysis (*45*, *46*), spectrographic, x-ray spectrographic and radiometric analysis (*132*); and such typical micromethods (*41–43*) as the use of the coloroscopic capillary, the borax bead, and the textile fiber test, permitting the identification of a few thousandths of a milligram (γ) or less. The typical microchemical tests and methods of separation and identification of Emich (*41–43*), which have proved of wide general application (*18*), have been modified and applied to work on a semi-microscale by Engelder (*44*) and others (*131*), eliminating the use of a microscope altogether. Noteworthy are the recent contributions to qualitative inorganic microanalysis by Benedetti-Pichler (*14*), Schoorl (*123*), and Whitmore (*144*).

ORGANIC. For the qualitative elementary analysis of organic compounds, tests of almost similar sensitivity have been worked out chiefly by Emich (*41–43*):

Carbon	0.001 γ ($CaCO_3$)		Nitrogen	5 to 10 γ	(Lassaigne's test)
Hydrogen	100 γ (H_2O)		Sulfur	1 γ	($BaSO_4$)
Nitrogen	0.1 γ (NH_3)		Halogen	10 γ	(Beilstein test)

Applications of qualitative microanalysis to organic compounds (identification of chemical species) are numerous; their number in biochemistry and physiological and pathological chemistry is legion. Important contributions in this direction have been made by Behrens (*11*, *12*), Chamot (*27*, *28*), Garner (*53*), Molisch (*98*), Rosenthaler (*119*), and many others (*60*, *61*). But taking into consideration that there are at present already 4877 homologous series of compounds known in organic chemistry (*112*), each series in turn comprising hundreds and even thousands of individual compounds (chemical species), all of which show more or less similar qualitative chemical characteristics, attempts in the direction of an all-embracing qualitative organic microchemical analysis meet with extreme difficulties. Studies to replace the general analytical procedures, the ordinal, generic, and specific tests of Mulliken (*100*), Kamm (*75*), Rosenthaler (*119*), and others (*53*) by equivalent microchemical procedures are already under way in this laboratory, using Emich's (*41–43*) centrifuge cone and capillary technic together with Feigl's (*45*) spot-analysis methods.

Quantitative Microanalysis

INORGANIC. Here again the methods of Emich (*41–43*) are of widest applicability (*79*). His method of three weighings is still the simplest. It involves the use of the inverted filterstick (*Filterstaebchen*) and the microbeaker, which are weighed together on a microchemical balance to the nearest γ. The sample is then introduced into the microbeaker and the ensemble weighed again. Then the solution, precipitation, and filtration are carried out in the same beaker and with the same filterstick and finally both are dried, or ignited, and weighed together (the third weighing). Since the beaker as well as the filterstick might be made of glass, quartz, or porcelain, the applicability of this method to most gravimetric inorganic analytical methods is obvious (*79*, *97*).

These methods have been further developed to include quantitative analysis of amounts of a few γ (*145*) and complete quantitative analysis of several elements in one single sample of a few milligrams weight (*13–18*, *66–68*, *133*). Quantitative microelectrolysis has received repeated attention (*145*) and the contributions of Clarke and co-workers (*31–34*) are of wide interest. Quantitative microanalysis of gases (*94*) has been further studied and perfected (*125*).

ORGANIC. As inorganic quantitative microchemical methods are not so widely used as their practicability would warrant, and as substitution by the various electrometric, spectrographic, colorimetric, and fluoroscopic methods may be resorted to, the quantitative organic microanalytical methods as first devised by Pregl (*89*, *113–115*) are today indispensable in any modern organic chemical research laboratory.

The microchemical balances necessary for this type of work must have a rather large weighing range (up to 20 grams) and yet should retain their sensitivity at this maximum load (*126*). Taking into consideration that a macrosample of 0.1 to 0.2 gram can be weighed on an ordinary analytical balance to ± 0.1 mg., which corresponds to a precision of ± 0.05 to ± 0.1 per cent, it will be necessary to weigh a microsample with the same precision. Since the average sample is between 3 and 5 mg., reproducibility of weighings must then be within at least 3 to 5γ, to give the same accuracy as in macroweighings. Reproducibility of weighings within ± 2 to $\pm 3\gamma$ is obtainable with the microchemical balances of Kuhlmann, Starke-Kammerer, Nemetz, Bunge, Sartorius, Becker, and others (*126*). Of interest are the latest investigations as to the possible improvements in microchemical balances by Donau (*38*) and Ramberg (*116*). Objects weighing more than a few grams, such as halogen filter tubes or the carbon and hydrogen absorption tubes, need not be weighed more accurately than to $\pm 10\gamma$, which further facilitates the application of many organic microquantitative methods. The necessary precautions include a solid foundation for the balance, and protection from immediate sources of heat, draft, or dust. Any chemical laboratory equipped for quantitative in-

organic macroanalysis ought therefore to prove suitable for quantitative organic microanalysis.

The most important method in quantitative organic elementary analysis is the determination of carbon and hydrogen, and this has received considerable attention in the past few years.

The original Pregl method with the two gasometers, without a preheater but with the double combustion gas line, has undergone several changes. For instance, the double combustion gas line has been eliminated by several workers (*102, 105, 143*); the side inlet (*99*) at the combustion tube and the preheater (*21*) constitute further improvements. The changes in regard to the actual combustion tube filling (*10, 62, 71, 78, 88, 89*) and the heating mortar (*139*) are fewer and do not appear to constitute a revolutionary deviation (*49, 50–52, 121*). That the use of electrically heated units (*49*) is at present preferred is to be expected. The original Pregl absorption tubes have been retained by most investigators, with Kemmerer and Hallett (*76*) and Cornwell (*35*) using mercury seals, while Boetius (*22*) prefers the insertion of copper or silver wires into the capillary constrictions, thus increasing the constancy of the tubes (*20, 71, 96*). Friedrich (*50–52*) devised two kinds of sealable absorption tubes, one type with revolving stopcocks and another with springs, to prevent the loosening of the stopcocks during the manipulations. Anhydrone and ascarite fillings for the absorption tubes were recommended by several investigators (*77–79, 102–109, 146*) and have been found highly satisfactory.

The sources of error are still rather numerous, as shown by Boetius (*22*), and therefore it was found desirable not only to use one combustion gas line (oxygen) for the combustion, but also to devise means for a separate control of the absorption train, whereby possible sources of error in this part of the apparatus are readily detected. Such an arrangement is used in this laboratory (*105, 109*); it has been found practical and has been tested out with inexperienced students and beginners. Similarly useful proved to be the setting up of two carbon and hydrogen apparatus, one having a combustion tube filling according to Pregl and one containing silver wool instead of the lead peroxide, to be used for compounds not containing nitrogen.

More radical changes in this combustion method were introduced by Lindner (*92, 93*), whose method makes it possible to determine both water and carbon dioxide by titration. Absorption of the carbon dioxide with barium hydroxide and gravimetric determination of the barium carbonate formed were tried by Niederl and Meadow (*104*). In this method amounts of about 0.5 mg. were found most suitable and analyses were performed on amounts as minute as 0.02 mg. with a precision of ±1 per cent.

Of later date are the wet-combustion methods of Dieterle (*37*), Lieb (*90*), and others (*26, 31–34*), in which the carbon dioxide is determined by titration. The manometric method (*86*), especially the method of Van Slyke (*138*) which permits the quantitative determination of carbon in samples weighing less than 1 mg. with an accuracy of ±1 per cent, appear advantageous.

Although the above methods permit the determination of carbon only, there are nevertheless reports in the literature of methods in which not only carbon and hydrogen but also oxygen (*80*), sulfur, and halogens (*50–52*) are determined simultaneously. A more detailed summary of recent investigations in the quantitative microdetermination of carbon and hydrogen has been given by Boetius (*22*), Weygand (*143*), and Niederl (*102*).

The microanalytical determination of nitrogen by the Dumas method as devised by Pregl is one of the most satisfactory (*69, 101, 140*). No important changes have been introduced. The empirical correction of 2 per cent was investigated (*108, 135, 136*) and found to be composed of several factors, such as that due to the residual air in even the purest carbon dioxide, the adhesion and vapor pressure of the 50 per cent potassium hydroxide solution, and the air absorbed by the temporary filling of copper oxide. The residual air in the carbon dioxide appears to be the most important factor and therefore the use of measured amounts of carbon dioxide from a graduated gasometer seems to be of advantage. Using aliquot portions of macrosamples, this method does not necessarily require a microchemical balance. This same advantage in a higher degree is shown by the micro-Kjeldahl method for the determination of nitrogen (*73, 124, 125*). The original apparatus of Pregl and Parnass-Wagner has undergone little change and the relative simplicity of the procedure made possible an early development of an ultra-method by Kirk and co-workers (*56, 77–79, 97*). Interesting are the many fruitful attempts to widen the scope of applicability of this method, which usually is limited to aminoid nitrogen. By suitable introduction of reducing agents [glucose (*40*), hydriodic acid (*50–52*)], nitro and nitroso compounds may be analyzed satisfactorily.

The number of the quantitative microanalytical methods for the determination of halogens and of sulfur has been enlarged (*19, 70*) by the introduction of the Parr bomb (*8, 39, 53*), a wet-combustion method (*90, 148*), and procedures permitting the volumetric determination of these elements (*141, 146*).

In the microdetermination of molecular weight very few changes have been introduced. The simple cryoscopic method of Rast (*117*) has been adapted for liquids (*74*) and also a variety of new solvents with high molecular depression constants have been found (*111*). The ebullioscopic method of Pregl (*113–115*) formed the basis for the micromolecular weight method of Rieche (*118*). Extremely simple is the vaporimetric method by Niederl (*102*) and co-workers (*106, 107*), while the comparative osmotic pressure method of Barger (*9*) still enjoys a wide use. Rather novel in molecular weight determination methods are the *schlieren* experiments of Emich (*41–43*), based upon the experimental fact that solutions of equal refractive index, but containing solutes of unequal molecular weight, exhibit double *schlieren*, whereas solutes of equal molecular weight under the same experimental conditions do not.

The precision normally obtainable by these micromethods is shown in Table I.

Table I. Precision Obtainable by Micromethods

Kind of Determination	Allowable Error
	%
Metals	±0.2
Carboxyl	±0.5
Nitrogen (Kjeldahl)	±0.1
Nitrogen (Dumas)	±0.1
Carbon and hydrogen	±0.3
Halogen	±0.2
Sulfur	±0.2
Molecular weight	±5

The methods for the determination of atomic or molecular groupings in organic compounds have undergone several changes. Notable improvements were made in the determination of alkoxy and alkyl imide groups (Vieboeck, *141*) and the determination of acyl groups (*51, 87, 115*). Another important addition is Roth's (*120*) microdetermination of active hydrogen based on the corresponding macromethods of Zerewitnoff.

Not mentioned in this paper are the enormous numbers of microanalytical methods for known substances in mixtures and solutions used in medicinal (*95, 137*), biological, physiological, and pathological chemistry.

Microtechnic of Isolation and Purification

The progress of microchemical technic has by this time reached a state where, according to Benedetti-Pichler, it can be said that 1 mg. of sample, either liquid or solid, is sufficient for a single chemical or physical operation, such as determination of melting point, boiling point, specific gravity (*58*), molecular refraction, solubility, and several qualitative or one quantitative elementary analysis.

For procedures involving several steps, such as are encountered in organic syntheses, larger quantities are still

needed at present, the lower limit being 10 mg., whereas 50 mg. constitute the average amount of material, permitting not only purification but also complete quantitative elementary analysis (carbon and hydrogen, nitrogen, halogen, sulfur, etc.), the determination of the molecular weight, specific rotation (*47*), and the preparation, purification, and complete analysis of a suitable derivative. Examples of the successful application of these decamilligram processes can be found in the modern organic chemical literature [Butenandt, Karrer, Koegl (*81*), Kuhn, Ruzicka, Wintersteiner, etc.].

Prerequisite to the application of quantitative structural analysis is a high state of purity of the compound under investigation. In choosing the methods of purification the amounts of material available and its state of aggregation, whether solid or liquid, have first to be considered. If the material is a liquid, purification by distillation will first be tried. The best micromethods for vacuum distillation (*113*, *128*) permit successful distillation of a few cubic centimeters, with 1 cc. of liquid about the limit. For distillation under atmospheric pressure, for amounts of about 0.1 to 1 cc., the distillation methods of Alber (*1–7*) can be successfully applied. For smaller amounts, 50 cu. mm. and less, the fractionation tube of Emich (*41–43*, *55*) is the most convenient tool, allowing a successful fractionation of 10 cu. mm. Determination of the boiling point is accomplished by the application of the Siwoliboff (*127*), Niederl (*106*), or still better, the Emich (*41–43*) method, the latter permitting the repeated determination of the boiling point without loss of as much material as 1 cu. mm. The *schlieren* method of Emich (*41–43*) and co-workers (*1–7*, *65*, *122*) is ideally suited to the determination of the purity of liquids.

Schlieren formation is due to differences of the refractive indices of the materials under investigation, giving positive or negative *schlieren* respectively, depending on whether the "flow sample" or the "stand sample" has the higher refractive index. Simultaneously minute differences in specific gravity can readily be determined, as indicated by the formation of falling or rising *schlieren*, depending again upon whether the flow sample or stand sample has the higher or lower specific gravity. Differences of 0.0001 in the refractive index and 0.001 in the specific gravity can thus be determined, with amounts of material of 50 cu. mm. for the stand sample and about 20 cu. mm. for the flow sample. For this type of determination the *schlieren* microscope as devised by Emich has been found suitable. The visual method of Alber (*1–7*) is very practical, also permitting quantitative determinations. Of special interest are the so-called double and colored *schlieren*, which are formed when solutions or mixtures of equal refractive indices are used, permitting the visual observation of such phenomena as molecular and ionic diffusion, heat of neutralization, enzyme action, etc. (Studies in intramolecular rearrangements of phenyl ethers by means of this method were carried out in this laboratory.)

The isolation and purification of solids necessarily involve extraction (*72*, *142*), crystallization, recrystallization, precipitation (*130*), reprecipitation, or sublimation (*29*, *48*). These methods, however, demand a preliminary examination of the material as to solubility, purity, homogeneity, and behavior on heating. All these preliminary investigations are most conveniently carried out with the aid of a polarizing microscope. Such examinations should not require more than 1 mg. of material and the technic of Behrens (*11*), Chamot (*28*), Emich (*41–43*), and others (*1–7*) are of the widest applicability in this respect. The determination of the melting point of a solid organic substance is a micromethod in itself and can be augmented and sensitized as shown by Kofler (*82–84*), using a microscope provided with an electrical heating stage, thermocouples, and other implements promoting the accuracy of such determinations. For recrystallization and subsequent filtration the arrangements devised by Pregl (*113–115*) are suitable for amounts of material from 50 to 100 mg., with 20 mg. being about the lower limit. For amounts below 50 mg. the use of Emich's (*41–43*) centrifuge cones is appropriate. For amounts not above 10 mg. his capillary technic appears the sole suitable method at present, permitting the crystallization, recrystallization, and determination of the melting point in one and the same capillary.

For the sublimation (*36*) of small amounts of solid material, various methods are in existence. For comparatively larger amounts, 50 mg. and above, the simple sublimation devices of Soltys (*129*) are entirely practical. For smaller amounts the procedures of Emich (*41–43*) or Chamot (*27*, *28*), involving the use of microsublimation chambers, capillaries, and microscope slides, are in order.

Microchemical Literature

Reports in the chemical literature of microchemical analysis and procedures go back to the first uses of the microscope for observation of chemical reactions. One of the first contributions in the United States was the monograph "The Microchemistry of Poisons" by Wormley in 1867 (*147*). Later the interest in this type of scientific endeavor continually increased, with the fundamental contributions of Behrens, Chamot, Emich, and Pregl as outstanding achievements. Table II might be taken as illustrative of the increased applications (*24*, *25*, *30*, *54*, *55*, *57*, *59*, *88*, *91*, *95*, *110*, *134*) and the development of the microchemical literature, which by this time has reached rather voluminous proportions.

Table II. Number of Microchemical Papers per Year

1890–1900	8	1925–1930	440
1901–1910	17	1931	850
1911–1919	102	1932	1500
1920–1924	140	1933	1800
		1934	ca. 2000

At present the majority of microchemical contributions are found in *Mikrochemie*, in the various biochemical and physiological chemical periodicals, and in Industrial and Engineering Chemistry, Analytical Edition. *Mikrochemie*, in addition to original contributions, presents systematically accurate résumés and compilations of methods and procedures (*Beihefte* and *Sammelreferate*), a procedure also adopted by the *Zeitschrift für analytische Chemie* (*Fortschrittsberichte*, *1–7*, *13–18*, *102*).

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The Role of Analytical Chemistry in Industrial Research

II. Microanalysis

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IN THE FIRST paper (*3*) of this series a general description was given of the analytical organization evolved at Bell Telephone Laboratories. The present paper is concerned with the unit of the organization that was termed in the first paper "microchemical analysis." The word "micrurgy" was coined by Petérfi (*12*) to describe biological microdissection and later expanded by Titus and Gray (*13*) to include dissection and examination under the microscope of nonbiological material. Since the term, by its pure Greek derivation, means "operations on a small scale or work with minute quantities," it can logically be used as a general term to include microchemistry, microanalysis, and chemical microscopy, as well as such special technics as those developed in the authors' laboratory and presently to be described. It is here so used, and is suggested for general adoption.

Moser (*10*) has emphasized the fact that until recent years analysis has not been a specialized branch of chemistry. This is true as to both apparatus and personnel. The classical methods of analysis evolved largely through the application of such reactions as were readily conceived on the basis of nonspecialized chemical knowledge. Comparatively little search was made for new reactions having specific advantages for analysis. Very few special pieces of apparatus were developed, and even today the glassware and other equipment seen in most analytical laboratories do not mark them off from laboratories devoted to other kinds of chemical work. Among the other shortcomings and disadvantages of classical analytical chemistry are: frequent disproportionality between the quantities of the elements sought and the size of the apparatus, causing large inherent errors; and, as Kirner (*9*) has pointed out, time-consumption, explosion hazards, and costliness of reagents in macroscale operations.

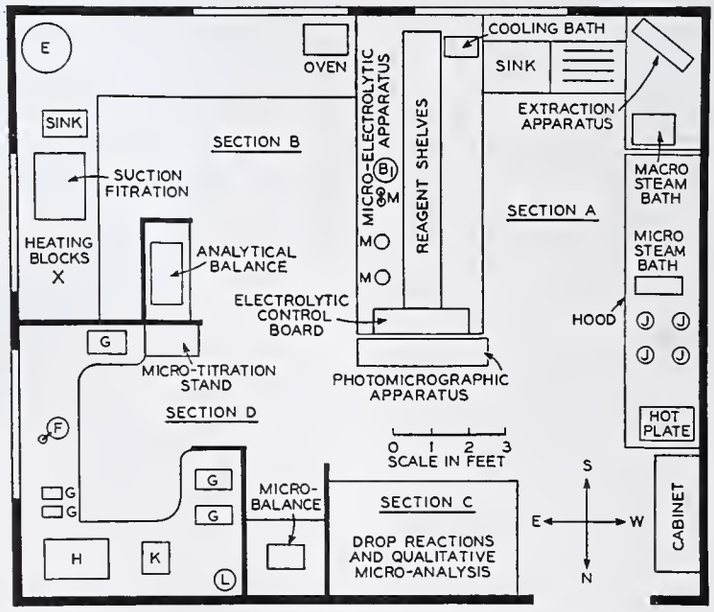

Figure 1. Plan of Laboratory

The application of microtechnic to industrial chemical problems is a recent development in the United States. A number of papers, such as those of Grassner (*7*), Niessner (*11*), and Goubau (*6*), have described the use of this technic in European laboratories.

Kirner (*9*), in a recent paper, has discussed the application of the standard Pregl methods of organic microanalysis to a specific industrial problem—research on coal at the Coal Research Laboratory at Pittsburgh. So far as the writers know, however, no description has appeared of an American laboratory designed to handle general problems in the examination of materials by micrurgical technic.

Such a laboratory has been evolved at Bell Telephone Laboratories (*8*). A number of industrial concerns, hearing of its work, have sent their chemists to inspect the laboratory, with a view to setting up similar facilities; others have written to the authors. The present paper is intended to make generally available a record of experience in this field.

Province of Micrurgy

Materials analyzed or examined by the Analytical Division fall into the following broad classes:

1. Electrical conductors
2. Materials used as electrical insulators or dielectrics
3. Magnetic materials
4. Protective and finishing materials
5. Structural materials
6. Transformation products
7. Miscellaneous

By "transformation products" are meant materials used in telephone apparatus and in the plant, that have undergone some deteriorative change with use. Chief among them are corrosion and tarnish products proper; also included are deteriorated rubber, insulating and lubricating oils, paper,

impregnating compounds, etc. Tests made on such materials are usually of a diagnostic nature: There has been a service failure, and the samples submitted are the material evidence from which it is desired to gather information as to fundamental causes and at the same time to deduce the proper preventive or palliative measures.

When a request for an analysis is accompanied by an adequate sample, and when the work to be done calls for standard procedures, the analysis is carried out in the General Analytical Laboratory by macromethods. Frequently, however, because of the delicacy of the necessary sampling or preparative operations, of the small size of sample, or of the complex character of the tests to be made, a requested analysis cannot be performed efficiently by a standard procedure. In these cases the use of micrurgical technic is indicated.

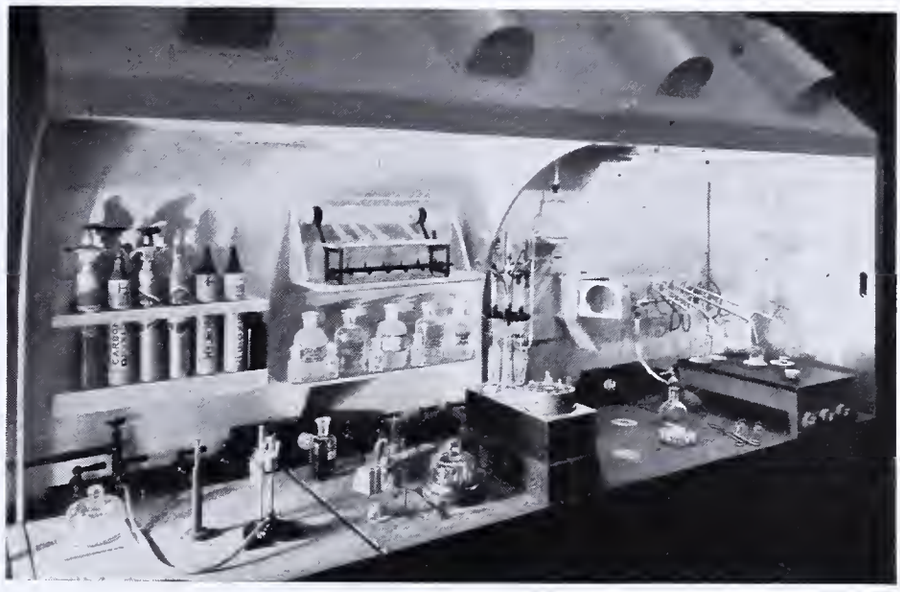

FIGURE 2. VIEW OF HOOD

Center, steam bath for microapparatus; right, air jets for aiding evaporation of liquids on hot plate.

Description of Laboratory

The objective was to design laboratory space suitable for general micrurgical work in which three or four men could work comfortably. Owing to the extreme dustiness of the air in lower Manhattan, it was immediately apparent not only that a special room must be provided but that some system of air filtration must be employed. While air filtration may not be necessary in localities where the air is cleaner, it is the authors' conviction that a special room is a prime requirement for good results. Similarly, the materials used to cover the walls, floor, and laboratory furniture should be chosen with the object of eliminating, so far as possible, dust sources within the room. Some of the work benches are covered with "battleship linoleum," a heavy grade of black-surfaced linoleum. Once a month the surface is refinished with beeswax. This material, besides its advantages from the dust standpoint, tends to reduce breakage; and the black background is desirable. Since, however, heating equipment would injure linoleum, benchtops carrying such apparatus are of stone. The laboratory floor is covered with "asphalt-asbestos tile."

Figure 1 is a plan of the laboratory. There is a general division of the space into four sections: for macropreparative operations, *A;* for quantitative microanalysis, *B;* for qualitative microanalysis, *C;* and for microscopic and general micrurgical work, *D.*

The hood has three removable partitions, so that operations can be segregated when desirable. A micro-Kjeldahl digestion stand is permanently placed in the hood. Into the back wall is built an assembly for treatment with hydrogen sulfide, supplied from a small tank of the "lecture bottle" type. An arrangement is provided whereby the gas can be passed with the same facility into a large beakerful of solution or a single drop on a microscope slide. The hood contains a steam bath, shown in Figure 2, with provisions for the steam-evaporation of liquids in microcentrifuge tubes of various sizes, microbeakers, etc. Capillary air-jets are used to aid evaporation both on the steam bath and on hot-plates.

A Becker microbalance having a rated sensitivity of 0.001 mg. is used. In order to minimize the effect on the balance of changes in temperature and humidity caused by the presence of the operator, the balance compartment is so constructed as to allow free circulation of air and yet to prevent sudden drafts. Mechanical insulation is effected in the following manner: The balance table consists of a slate slab on metal pipe legs which are insulated from the floor by rubber pads. A second slate slab rests on the table, supported by rubber stoppers. On this the balance case stands, its feet protected by Sartorius shock absorbers. A hood over the balance protects it from dust and air currents. A carefully centered light housing is built into the hood about 45 cm. (1.5 ft.) above the balance. A 1.25-cm. (0.5-inch) glass plate, ground on both sides, is interposed to absorb most of the heat. No trouble from unequal heating of the balance arms has been experienced with the particular balance in use. To avoid accidental jarring of the balance by the operator, a table top and apron are built around the balance on a level with the balance floor. These are attached to the partition and have no physical connection with the balance supporting structure.

FIGURE 3. MICRURGICAL SECTION

Left, one of reagent blocks, partly lifted out of its well.

A corner of the room, *D*, is equipped for the performance of general micrurgical operations. It is desirable to have available within a conveniently small working space facilities for applying the greatest possible variety of physical and chemical agencies to microscopic specimens. The determination of physical and optical properties, the study of structure, the mechanical separation and isolation of minute amounts of material, as well as such general operations as ignition, fusion, digestion, filtration, electrolysis, etc., may all be performed under the microscope with the special accessories here provided.

For chemical microscopy a Leitz petrographic instrument is used. It has been found to be a great convenience to have the microscope supported below the table in a well, *K*, of such depth that the stage is at bench level. Access to substage adjustments is through a sliding door at the front end of the well. When it is desired to use the microscope at bench level, a cover plate fits in the recessed edges of the well. The substage light is supported below the well, light being admitted to the microscope through a hole in the well floor. The substage light may be slid away and an arc light beam substituted when more intense illumination is desired. The arc light assembly is mounted horizontally on a rack near the floor, and may be slid to the back of the bench when not in use. The beam is bent vertically upward by a 45° mirror placed in line with the hole in the bottom of the well. Incident light is furnished by a Busch "punktlight" (tungsten arc bulb) supported on a ball joint above the well. When the microscope is used at bench level this may also be used for more powerful transmitted light, particularly when the image is to be projected on a screen. Close to the microscope a Reichert micromanipulator unit is mounted on a sliding base. The particular model was selected for its ruggedness of construction, a necessary requirement when relatively hard materials are studied.

Figure 4. Micromanipulator and Euscope in Use

A viewing screen (Bausch & Lomb Euscope) is also available for attachment to a permanently mounted adjustable supporting rod, so that both the micromanipulator and the illuminating devices may be used without change in the arrangements. This is useful for demonstration purposes and is particularly desirable where observations continued over a long period, as in dust counts, micrometry, etc., might otherwise result in eye fatigue. It also permits simultaneous observation of image and object being manipulated when more difficult operations are performed.

Solid reagents in 5-gram vials are kept in wooden blocks, stored in wells, *G*, in the table top where they are immediately available on removing the flush cover plates. This arrangement makes for neatness and compactness and reduces contamination from dust. Three wells are provided, one for inorganic solids, one for organic reagents, and a third for refractive index liquids. The two smaller wells shown in Figure 1 are for storing miscellaneous small equipment.

To avoid waste of time in setting up special equipment, a number of accessories have been installed permanently in the micrurgical section. A transite panel, *H*, set into the table top contains electrically heated aluminum blocks, a warm air jet universally inclinable for evaporation of liquids on microscope slides, and a quartz-lined muffle furnace of dimensions suitable for the ignition of microscopic specimens. The slides may be supported during preparation in the rubber-faced jaws of a spring clamp supported in turn on a ball joint. The slide may thus be inclined in any direction, a facility of considerable value in the decantation of drops and in evaporation with the air jet.

A group of flashlight cells controlled by a multipoint switch and a rheostat provides the small current necessary for carrying out electrolyses under the microscope, particularly with the cell described by Brenneis (*2*). Electrical controls for the various illuminators, heating devices and other equipment, and meters for the microelectrolytic circuit, are centralized on a switch panel at the back of the table.

A small high-speed centrifuge, *L*, with interchangeable heads for microtubes and capillaries is also conveniently available on the table. In order to avoid the deteriorating effects of acid fumes on delicate equipment, a miniature hood is provided, the draft through a hole in the window pane being maintained from the positive pressure of the air in the room. A sink of small dimensions, *F*, is provided by a Büchner funnel fitting into a circular opening with its edge level with the table top.

A dental motor with flexible shaft and a complete set of drills, burrs, stones, and cutting wheels is of invaluable service in procuring microsamples and in systematically reducing complex structures under the microscope. Dissecting tools are kept within easy reach in a wooden containing block. A Zeiss binocular dissection microscope is useful here. Its large stage permits the attachment of various accessory tools, clamps, etc., while the increased depth of focus and stereoscopic effect aid materially in carrying out manual operations.

Besides the microscopes mentioned above, a Zeiss research-type instrument is used for micrometric measurements and photography, while a portable-type Zeiss stand is available for field work where lightness and compactness are important.

On a bench in the east side of the room, back of the analytical balances, a group of small duralumin heating blocks designed for various purposes is permanently installed (Figure 6). Duralumin is preferable to other metals for this purpose owing to its high heat capacity and its nonoxidizability at elevated temperatures. On this same bench a ground-glass plate, sunk flush with the table top, contains a number of perforations each fitted with a flanged hard-rubber orifice and connected through its own valve under the table to the suction line. By placing a bell-jar with a filtering system inserted in its top over any of these suction outlets, a set-up for suction filtration is instantly available. An International clinical-type centrifuge, *E*, stands permanently in the southeast corner of the room. Bench B_1 is mainly used for microelectroanalysis, and cells of special design (*4*) are set up there. At the north end of the bench is a control panel on which are mounted switches, meters, etc., providing four circuits which can be simultaneously used. Concealed wiring leads to the four electroanalytic cell stations, *M*, on bench B_1.

Figure 1 does not show the outlets for water, gas, pressure, and vacuum, which are conveniently placed. Storage space is provided by cabinets and shelves above and under the benches and on the walls. In an effort to conserve bench space and eliminate cumbersome equipment, the ordinary ring stand supports have been replaced by steel rods which fit into tapering bores of flush sockets, several of which are installed on each bench. Bunsen burners are permanently mounted below the table top in the hood, 6-cm. (4-inch) holes, *J*, with removable flush cover plates providing access to the flame and support for clay chimneys, triangles, etc. Tripods and stands are thus eliminated.

In micrurgical work especially the apparatus is usually built around the job. It is therefore essential that facilities for working in wood and metals, as well as for glass-blowing, be available. The authors employ for this purpose a room adjoining the micrurgical laboratory. Here also is installed equipment for grinding and polishing specimens.

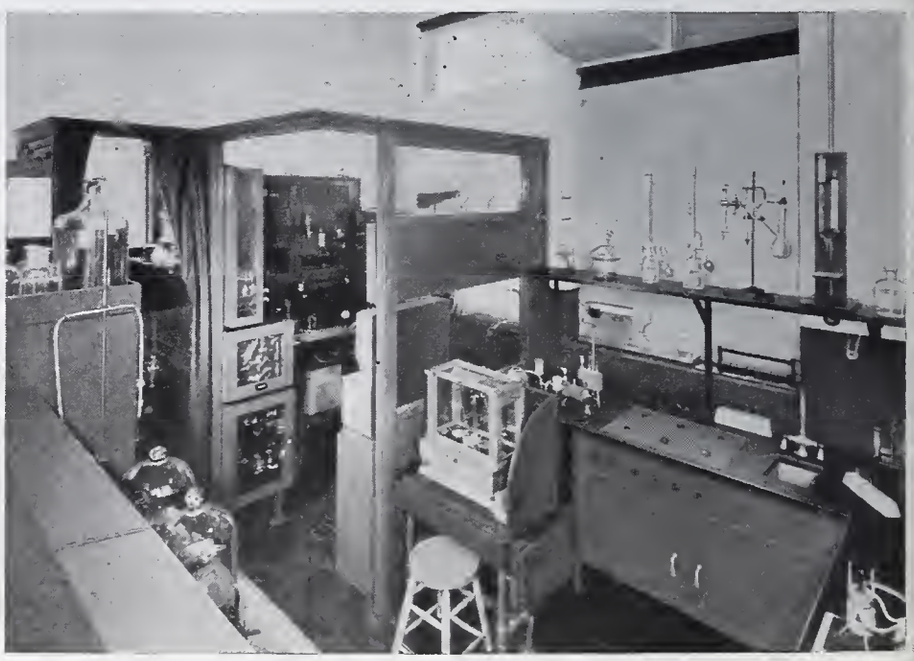

Figure 5. Southeast End of Room

In addition to the apparatus and equipment mentioned, and to other standard microchemical equipment, the following items, for the most part original with the authors and to be described in separate papers, are used in the micrurgical laboratory:

Sublimation apparatus
Stage furnace
Magnetic stage
Hot wire for use under microscope
Sedimentation devices
Steam-jacketed wells for evaporation of drops
Dilatometer for gasometric microanalysis
Microdistillation apparatus
Microextraction apparatus
A unit containing a quartz microfurnace, in which small specimens may be treated with various gases and the gaseous products analyzed
Leitz colorimeter and nephelometer
Apparatus for dust collection and analysis

Examples of Use of Micrurgical Technic

The examinations carried out in the micrurgical laboratory are of the most varied nature, as to both the materials studied and the technics employed. By contrast with most microchemical laboratories the authors deal little with the elementary analysis of pure organic compounds. The following is one method of classifying micrurgical technic:

General Technics

1. Identifications by reactions carried out under the microscope.
2. Identifications by "spot tests," using specific color reactions and indicator papers.
3. Quantitative analysis of organic and inorganic materials in which usual analytical operations are reduced to microscale.
4. Identification of organic compounds facilitated by micromethods.
5. Quantitative organic analysis by Pregl methods.
6. Diagnostic studies and chemical differentiation of microstructure in complex materials.
7. Identification of materials based on recognition of microstructural features.
8. Studies of grain and crystal forms of powders, precipitates, etc.
9. Micrometric studies.
10. Preparation of small amounts of substances either too rare or too dangerous to be handled on larger scale.

Special Technics and Applications

1. Diagnosis of corrosion causes.
2. Identification of surface contaminants, such as tarnish films, compacted deposits, efflorescent products, etc.
3. Composition studies made on thin layers or localized areas to determine degree of nonhomogeneity of materials.
4. Dust analysis.
5. Analysis of air for gaseous impurities.
6. Identification of foreign inclusions and segregations.
7. Application of improved methods for determining impurities.
8. Transformations in materials best observed on a microscale.

Two examples, taken from the authors' laboratory records, will illustrate the types of problems in which micrurgical methods are effective.

Contact points of various metals and alloys are widely used in telephone apparatus, as in relays and switches. Rapid qualitative analyses are frequently required to identify the alloy. Usually only a single contact is available and this must not be destroyed. Sufficient sample is obtained by drawing the metal across a roughened spot on a microscope slide. The resulting streak is dissolved in acid, transferred to a clear glass slide, and evaporated. Identification of this residue is made by reactions carried out under the microscope. If a quantitative analysis is desired, samples may still be removed without destroying all of the contact point by means of the dental engine using a tiny rounded burr. The operation is carried out under the microscope, the drillings being retained by a drop of oil from which they are subsequently recovered by centrifuging and washing with a suitable oil solvent. The quantitative analysis of such minute samples employs specially designed microapparatus, such as weighed microbeaker and inverted filter units or centrifuge tubes, and the microcolorimeter.

The micrurgical laboratory is frequently called upon to diagnose cases of high contact resistance. Some of these were found to be caused by the entrapment of foreign particles, as of dust, between the points. This led to an elaborate study of the nature and origin of dust in central office air, involving nearly the whole range of micrurgical technic.

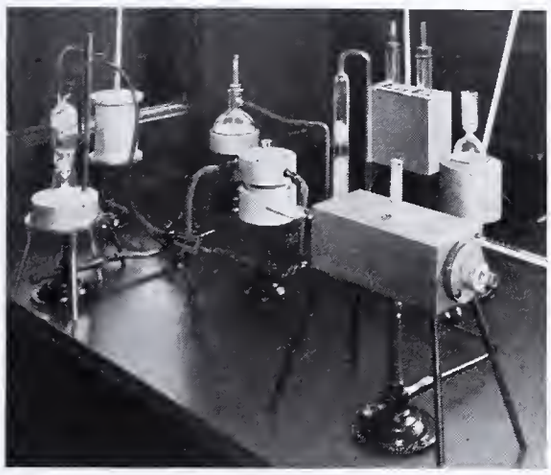

Figure 6. Duralumin Heating Blocks

When tarnish films or corrosion products are found to cause the trouble, an attempt is made, by considering the method of manufacture of the apparatus and its service environment, to determine the primary cause. In one case welded silver contacts developed high resistance. An extremely thin tarnish film was detected on the silver. Sulfide was demonstrated by the sodium azide catalytic reaction of Feigl, and confirmed by the formation of cadmium sulfide with cyanide solution containing cadmium. The presence of copper was made strikingly evident by pressing the contact points on ammoniacal diethyldithiocarbamic acid test paper. The weight of the tarnish film on one of these contacts was not more than a few ten-thousandths of a milligram. The copper contamination probably came from the welding electrode.

The other example is the analytical examination of lead cable sheath. Because of the large amount of this material used by the Bell System, and of its essential protective function in the telephone plant, constant effort is made to develop improved alloys, to perfect manufacturing methods, and to reduce cable losses caused by corrosion of the sheath. Micrurgical methods of analysis are of great service in all this work, but particularly in diagnosing cases of cable sheath failure. When the sheath is corroded it is necessary to distinguish between the different types of chemical and electrolytic corrosion, and, in seeking the cause, to examine the environment. Lead peroxide, chlorides (anodic products), and free alkali (cathodic), in abnormally high concentration, are indicative of electrolytic corrosion. Such substances are quickly and graphically detected by specific indicator papers. The flattened specimen is pressed against moistened phenolphthalein, silver chromate, and benzidine acetate papers in the order named. Photographs of the original specimen and the corresponding prints provide a permanent record of the examination. The structure of the different zones and layers of the specimen, revealed by dissection with the micromanipulator and analytical study, gives information that aids in reconstructing the mechanism of the corrosion process.

Discussion

The purpose of special analytical technics is to increase the economy of analysis. Emich (*5*) has enunciated this as a general principle:

> Auf allen Gebieten menschlichen Schaffens kommt dem Prinzip der Ökonomie die grösste Bedeutung zu.
> Dieses Prinzip verlangt bekanntlich, dass man sich bemühen muss, ein gegebenes Ziel mit einem Minimum von Material- und Energieaufwand, von Zeit und von Denkarbeit zu erreichen.

Perhaps the most characteristic feature of micrurgy is its employment of direct observation instead of inferential deductions from indirect observations. The organic chemist, wishing to determine the position of a substituent, is not able to make direct microscopic observation but must rely on circumstantial evidence. Similarly, a paper chemist, if limited to macroanalytical methods, might conclude from analyzing the ash of two condenser papers that the one with the higher iron content would be functionally the poorer. But micrurgical examination of the papers might disclose that the one with lower iron contained actual metallic particles, greatly reducing the breakdown resistance, while the iron in the other was evenly dispersed as the relatively innocuous iron oxide. Again, a lead-cable-sheath corrosion product, examined by "test tube" methods, might show no active ion, and the analyst would be at a loss to diagnose the corrosion cause. Under the microscope, however, tiny pockets might be found which contained a high chloride concentration, easily detected micrurgically because the test is made *in situ* and not after dilution below the sensitivity of the test. Many other similar instances could be given where analytical data are useless or even misleading when the factor of distribution is not taken into account. Many materials are made up of minute structural elements, upon the nature and interrelation of which depend most of their gross mechanical properties. In such cases micrurgical methods are necessary no matter how large the available sample. Petrographers and metallographers preceded analytical chemists in recognizing the importance of this in analysis.

Conclusions

1. Directors of analytical laboratories should strive to provide at least some facilities for the use of all analytical technics, so as to allow some freedom of choice in a given problem.
2. The natural tendency is to use samples and apparatus of a size convenient to handle. The principle should be inculcated that following this tendency is often the way of inefficiency and sometimes results in gross error. The analyst should shape the apparatus and methods to the job, not to his hands. While the authors cannot fully agree with Benedetti-Pichler (*1*) that no special skill is necessary for the use of micrurgical methods, it is certainly true that much good micrurgical work can be done by any conscientious, well-trained analyst.
3. Teachers of microanalysis should impress upon their students that the operations of sampling and preparation in industrial micrurgy frequently require more time and skill than microchemical tests proper.
4. Finally, the authors would urge manufacturing engineers and research directors to adopt a more critical attitude towards analytical results. They will thus come to appreciate both the possibilities and the limitations of chemical analysis, and will be able properly to appraise the value of analysis to manufacturing and research. The prestige of the profession of analytical chemistry will not suffer from this appraisal.

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An Efficient Vacuum Pump Check Valve

ROY L. MOBLEY

Lacto-Yeast Co., Inc., Baton Rouge, La.

In many instances the laboratorian is not aware of the availability of mechanical devices of professions associated with his, and their most efficient adaptability to his purposes. Such an instance is evident in the use of the water-operated vacuum pump. Of the valves used for this purpose, none have ever consistently filled the requirements over any period of time. The writer, constantly working with this type of laboratory apparatus, desired a perfected valve, which was easily had by using simple pipe and fittings with a ball-check valve.

The materials required include one 0.125-inch brass ball-check valve, one 0.125 × 3 inch brass nipple, one 0.125 × 8 inch brass nipple, and two 0.125-inch brass street ells.

Determine the direction of flow through the valve and start the street ells in either end. Then insert the shorter nipple in the exit ell and the longer in the entrance, so that the longer of the two will be placed in the trap bottle and the shorter will lead to the pump. Tighten the joints well with a wrench, being sure to leave the valve in its upright position and horizontally in the assembly, otherwise it will not work. Then insert in the stopper of the trap bottle and connect to the pump by means of tubing. The trap serves as a further safety device, should the valve leak a bit.

Such a valve has given very satisfactory service when used on a pump maintaining from one to three funnels under a vacuum of 10 to 20 inches of mercury.

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Photoelectric Colorimetry in Microanalysis

Photoelectric Methods in Macro- and Microanalysis

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Photoelectric methods afford precise means for investigating colorimetric reactions. Most of the methods are in the range of microanalysis. The highest precision is undoubtedly afforded by the vacuum photoelectric cell-amplifier method. Barrier-layer cells are precise but considerably simpler. Either method can be made to yield data of fundamental importance.

OPTICAL methods have enjoyed widespread use in analytical chemistry in the past and no detailed explanation of the importance of the microscope, refractometer, polarimeter, or spectrograph as an analytical tool is necessary. Colorimetric analysis has been employed either for its convenience and rapidity, or for the estimation of traces of substances for which the ordinary gravimetric or volumetric methods are inadequate. There has been a feeling in some circles that colorimetric methods are necessarily crude and approximate and are likely to lack specificity to the extent that their employment is resorted to with reluctance and only because other methods fail. The adaptation of photoelectric photometry to the needs of colorimetry has introduced a new point of view and promises to revolutionize the field; progress in physical photometry has been so great that we are already in possession of instruments yielding measurements far more precise than the most exacting requirements of the analyst. If we accept the thesis that photoelectric photometry is already in the class of precise physical measurements and that the near future will offer even more refined and convenient means, it then becomes necessary to reëxamine colorimetry and see in what direction further research is desirable.

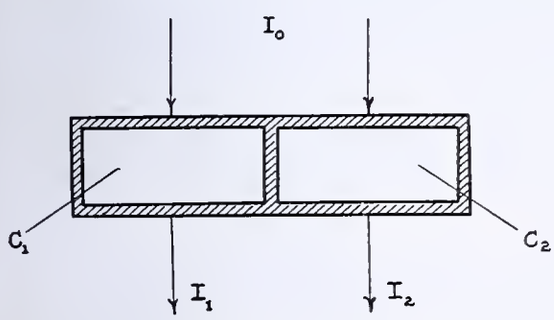

FIGURE 1. PHOTOELECTRIC MEASUREMENT OF INTENSITY

This paper shows definite results which have been obtained in the author's laboratory with photoelectric methods, and indicates the general lines along which future progress may be expected.

Ordered progress in the field will require, more and more, the elimination of empirical methods. The primary consideration is to establish conformity to the Lambert-Beer law. This fundamental relationship should form the basis for every exact colorimetric method. With due care, and insistence on this guiding principle, rigorous procedures and reliable instruments can be devised. The visual colorimeter, as embodied in the Duboscq type, employs this principle:

$$I = I_0 e^{-kct}$$

With initial intensity of light I_0 incident on both cups, containing solutions of concentration c_1 and c_2, adjusted to such depths of liquid t_1 and t_2 that the emergent light intensities I_1 and I_2 are equal, we have

$$I_0 = \text{const.}$$
$$I_1 = I_2$$

Therefore,

$$c_1 t_1 = c_2 t_2 \quad \text{or} \quad \frac{c_1}{c_2} = \frac{t_2}{t_1}$$

Photoelectric methods can be adapted here with little change; the cell merely replaces the eye and decides when the fields are matched. If we are concerned with the more usual photoelectric procedure of keeping the thickness constant and measuring the intensities I_1 and I_2, then the same law is used in a different manner (Figure 1).

Since $I_1 = I_0 e^{-kc_1}$
and $I_2 = I_0 e^{-kc_2}$

Therefore $\log \frac{I_1}{I_2} = K(c_2 - c_1)$

If we simplify matters by using pure solvent in one compartment and designating the light which emerges from this cell as I_0, then the intensity I which emerges from the compartment filled with colored solution of concentration c, will be given by

$$I = I_0 e^{-kc}$$
$$\text{or } \log \frac{I}{I_0} = -kc$$

Since I/I_0 is the transmittancy, we can write $\log T = -kc$.

The various forms which the expression takes can be summarized as follows

$$\log \frac{I_0}{I} = kc \qquad (1)$$

$$\log \frac{I}{I_0} = -kc \qquad (2)$$

$$\log T = -kc \qquad (3)$$

Convenient modes of representation are shown in Figure 2. D shows a very useful method of employing semi-logarithmic coördinates. If now, the respective intensities are measured by a photoelectric cell, in which the current is strictly proportional to light intensity, this graph will give the simplest relationship of all. Let the indicating instrument read 0 to 100 and adjust it to give full-scale reading when the compartment containing pure solvent is placed in the light beam. When the colored solution is placed in the same position, the photoelectric current will decrease to some value, T. This is the transmittancy directly and gives the ordinate value immediately. All subsequent values will be a linear function of c on the semi-logarithmic scale.

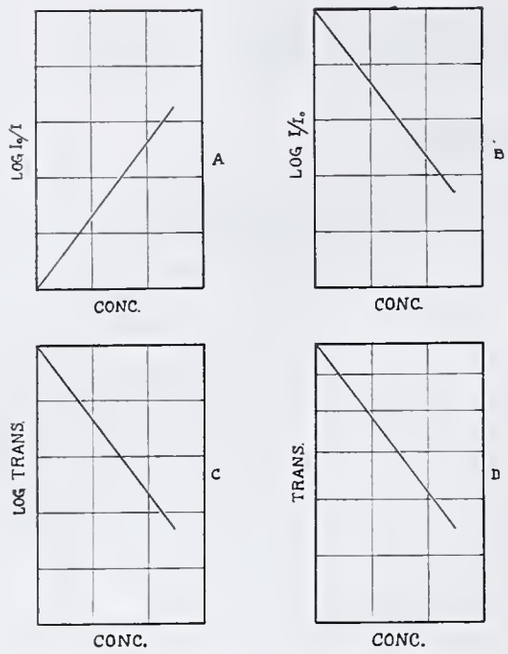

FIGURE 2. GRAPHICAL REPRESENTATION

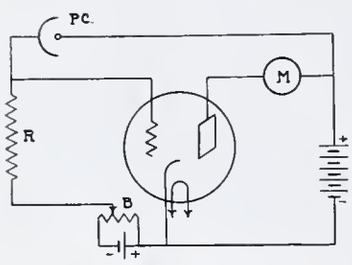

FIGURE 3. PHOTOELECTRIC COLORIMETER ARRANGEMENT

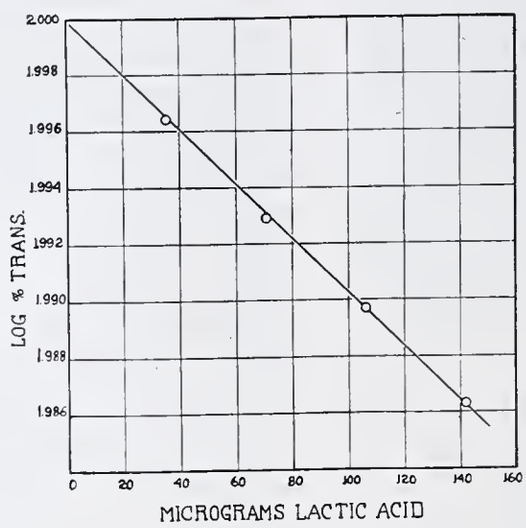

FIGURE 4. SENSITIVITY ATTAINABLE

It has been assumed throughout that the light employed is monochromatic. Indeed, the value of k depends on the wave length and may assume any value at every wave length throughout the spectrum. In order to conform to the requirements, light filters must be used, which will isolate comparatively narrow spectral regions. With very few exceptions (solutions of rare earths, etc.) the absorption bands of colored solution are broad enough to make this mode of isolation feasible. It is almost self-evident that the measurements will be most precise if the light which is used for photometry coincides with the region of maximum absorption of the solution. In careful work this region of maximum absorption is determined with the spectrophotometer. A filter can then be selected which transmits chiefly in this interval. Typical examples of this procedure are given below.

Before discussing the other physical and chemical factors which are important in precise colorimetry, some of the instruments suitable for photoelectric measurement will be described.

Photoelectric Colorimeters

No attempt will be made to exhaust the possibilities in circuit arrangement or choice of method, as these are treated very thoroughly in several texts and individual papers (*1*, *5*, *7*). Instead methods and instruments devised and investigated in this laboratory will be discussed as well as some of the results achieved. From the optical point of view the author has adopted the general procedure of using a twin absorption cell in which first one and then the other cell can be placed in the light beam, thus giving the ratio of the intensities of the transmitted light. If a vacuum photoelectric cell is used under proper conditions, the photoelectric current will be directly proportional to the light intensity. If such a measurement is made for the pure solvent and then for the colored solution, the values of I_0 and I so obtained will be related to c, as given in Equations 1 to 3. The photoelectric currents obtained under such conditions are very feeble, and for practical purposes should be amplified. Figure 3 shows a suitable arrangement. With constant illumination on the photocell, the introduction of a light-absorbing medium will cause a decrease in current in M. The tube bias arrangement, B, provides a suitable initial setting, and an alternative method of measurement. In place of B, or in conjunction with it, a precision potentiometer may be used. Any change in illumination can be compensated by the potentiometer until the original reading on M is restored. The compensating potential will be directly proportioual to the change in illumination. With no added refinements the circuit shown has been used in this laboratory for the colorimetric determination of hydrogen-ion concentration (*1*, *5*, *7*) for performing titrations automatically (*4*), and in the analysis of some organic acids (*6*).

Figure 4 gives some idea of the sensitivity attainable. (The color was produced by adding ferric chloride to lactic acid.) Over the range 0 to 142 micrograms, Beer's law is obeyed closely. At the highest concentration the relative light transmission is still 97 per cent.

The most precise results can be expected, in the light of recent developments

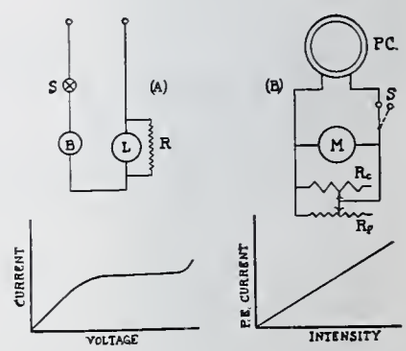

FIGURE 5. DIAGRAM OF PHOTRONIC CELL INSTRUMENT

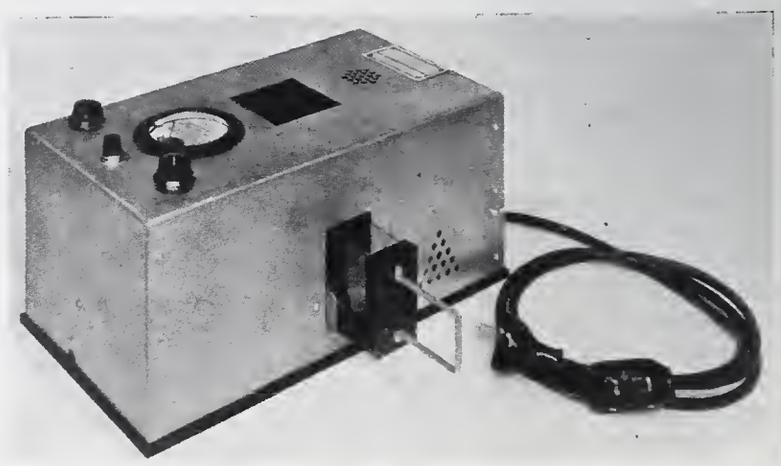

FIGURE 6. PHOTOGRAPH OF INSTRUMENT

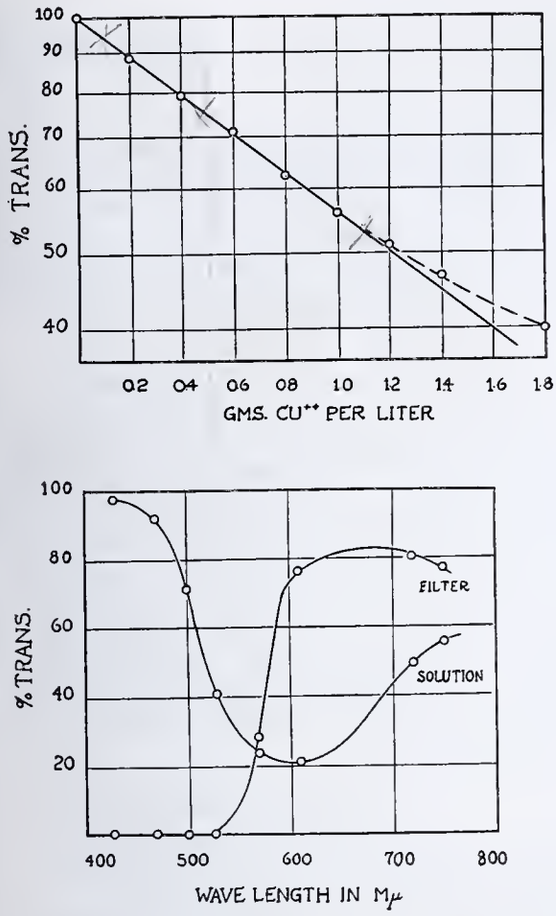

FIGURE 7. DETERMINATION OF COPPER AS CUPRAMMONIUM ION

in tube design and new circuits. These have all been in the direction of greater sensitivity and stability. Many investigators, however, avoid vacuum tubes almost instinctively, and prefer more direct methods. Such are available in the barrier-layer cells, of which the photronic cell is typical. The author has studied these cells in detail and the following description of an instrument using such cells is offered, not as the only one which has appeared, but as one which conforms to reasonably fundamental principles.

It is designed to operate from 110-volt alternating or direct current. Figure 5 *A* shows the light source, *L*, a switch, *S*, connected in series with a ballast tube of the iron-wire-in-hydrogen type. The ballast tube has operating characteristics similar to *c*. The resistor, *R*, shunting the lamp may be necessary to bring the load up to the flat operating portion of the ballast tube characteristic. This arrangement keeps fairly constant light intensity, but possesses some lag, and will not accommodate sharp transients. The measuring circuit consists of the photronic cell, *PC*, a switch, and two shunting resistors for the microammeter *M*, which provide for coarse and fine adjustment of the meter reading. Under conditions of low external resistance, the current from the photocell is strictly proportional to the light intensity (*2*). (Since we desire the complete elimination of arbitrary, empirical relationships, this method is preferred to balanced cell arrangements and other schemes which have been proposed, which may be very sensitive and suited to the problem in hand, but cannot add anything fundamental to precise colorimetry.)

The optical arrangement consists of the light source backed by a spherical mirror, a short-focus lens which renders the beam parallel, and a holder for a suitable light filter. A twin absorption cell movable at right angles to the optic axis carries the solution to be measured and the pure solvent. A second lens focuses the emergent light on the photronic cell. Figure 6 is a view of the instrument.

Figure 7 is illustrative of the procedure followed.

In determining copper as the cuprammonium ion, the absorption spectrum was first determined with a Zeiss gradation photometer. (This is sufficiently precise for most work. The author has made duplicate measurements on the Bausch and Lomb spectrophotometer from time to time, but wherever closer spectral resolution of this kind is required it usually happens that no suitable filter will be found which is satisfactory. Only the rare earths or other compounds having sharp bands fall in this class.) A light filter was then selected which transmits principally in the region in which maximum absorption is exhibited by the solution. In this case the filter selected was a Corning No. 348H.R. red shade yellow 4.29 mm. Solutions containing various amounts of copper were then treated with excess ammonia, made up to volume, and photometered against distilled water. With the water cell in position, the meter was adjusted to read full scale. (The meter is calibrated to read 0 to 100 and is labeled "per cent transmission.") Upon moving the other compartment into position, the meter reading then dropped to some value which indicated the per cent transmissions directly. These values are plotted on a logarithmic ordinate against the corresponding concentrations. Under these conditions conformity with Beer's law was obtained up to a concentration of about 1 gram of copper per liter.

The advantage of the linear relationship is apparent. Over the useful range the average slope can be computed, and in all subsequent analyses the concentration can be computed very simply. The ease of checking is obviously more straightforward and direct with the linear behavior. The author has spent several years in investigating the more important colorimetric methods in this manner and, while it is a bit laborious to determine all the absorption spectra and select suitable filters, it does reduce subsequent work with these systems to a simple and direct basis. (Many of the methods

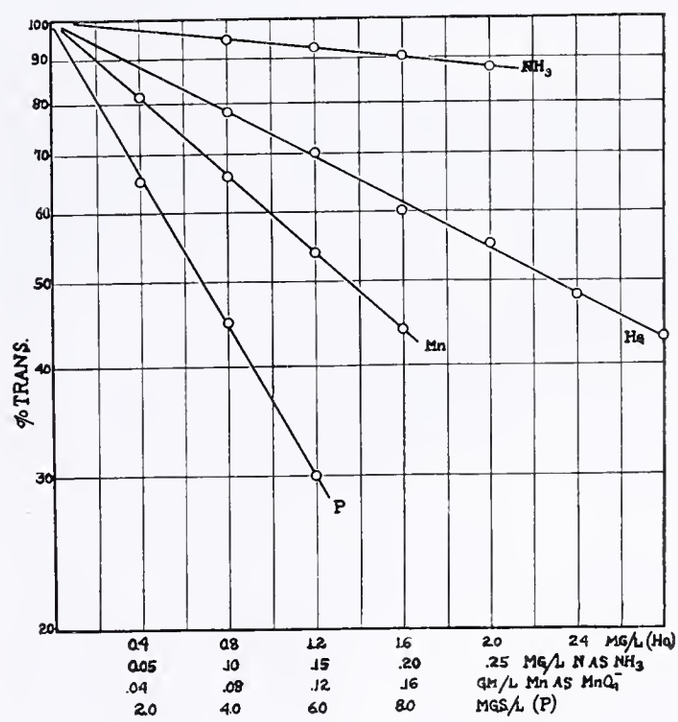

FIGURE 8. REPRESENTATIVE CASES, USING COLORIMETRIC METHODS

mentioned here will be described in separate papers in which the full details will be given.) Figure 8 shows some representative cases. The upper line shows the determination of nitrogen as ammonia by Nessler's reagent; the next, mercury by diphenyl carbazide; the third represents manganese as the MnO_4^- ion after oxidation with periodate. Phosphorus was measured by reduction of phosphomolybdic acid with sulfite and hydroquinone.

These examples may suffice to show that existing colorimetric procedures may be utilized in the photoelectric method to give results which conform to the fundamental requirements of optical laws.

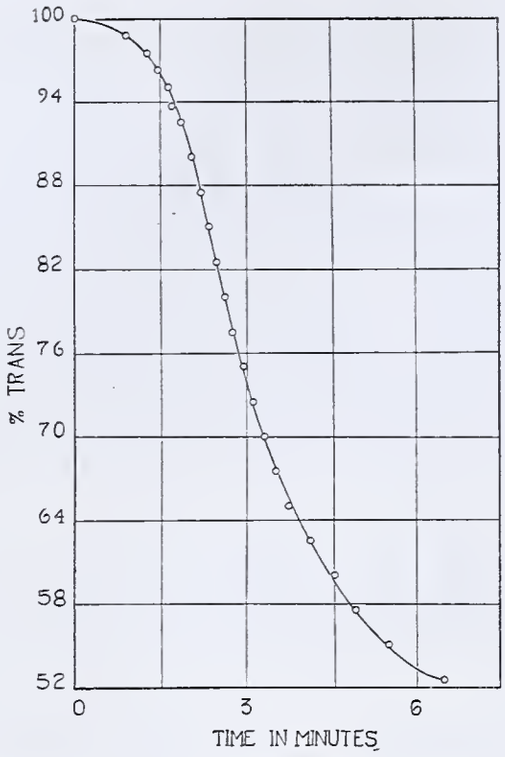

FIGURE 9. PHOTOELECTRIC MEASUREMENT OF RATE OF REDUCTION OF AURIC ION TO COLLOIDAL GOLD

Applications

It is common knowledge among analysts that the directions for many colorimetric methods include factors such as the "time for full development of color," or the "rate of bleaching." The photoelectric method is particularly suited to the study of these factors. Figure 9 illustrates a typical case, and records the rate of formation of colloidal gold. The reducing agent in this case was hydrogen peroxide. In the course of 6 or 7 minutes it was possible to record more than twenty values for the progress of the reaction. The kinetics of these reactions are important and yield valuable information.

It is often desirable to titrate extremely dilute solutions or to titrate in the presence of considerable background color. Electrometric methods are often enlisted in such cases, but the photoelectric method is useful also. Figure 10 illustrates the precise evaluation of the end point in a titration. The logarithmic plot gives the intersection of two straight lines as the determining agency.

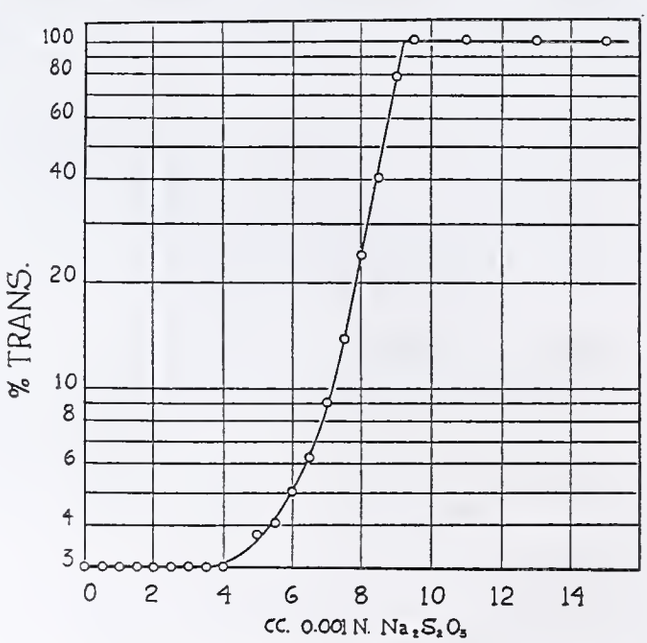

FIGURE 10. PHOTOELECTRIC TITRATION OF IODINE WITH SODIUM THIOSULFATE (STARCH INDICATOR)

The analyst is often confronted with the problem of identification rather than complete analysis. A case in point is the identification of an alloy. Even a minute streak on porcelain will provide sufficient material for a colorimetric test. If the ratio of two constituents is obtained quantitatively by photometric measurement, identification is possible even though the weight of the sample is unknown.

New Instrumental Methods

Two methods have been described which are suitable for precise photoelectric colorimetry. It may be of interest to mention a new development affording further simplification. Since the photoelectric current varies logarithmically with the concentration, it is a comparatively simple matter to feed it into a vacuum-tube voltmeter which has a logarithmic input characteristic and get an output which is a linear function of the concentration (*3*). An instrument of this type has been developed in this laboratory (*3a*). The same result can be achieved with the photronic cell, since the open circuit e. m. f. is a logarithmic function of the light intensity over a limited but rather wide range.

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RECEIVED March 12, 1935. Presented before the Division of Physical and Inorganic Chemistry, Symposium on Recent Advances in Microchemical Analysis, at the 89th Meeting of the American Chemical Society, New York, N. Y., April 22 to 26, 1935.

Developments in paper testing during 1934 are reported by B. W. Scribner of the National Bureau of Standards in the *Paper Trade Journal*, May 2, 1935. This is the annual report of the chairman of the Paper Testing Committee, Technical Association of the Pulp and Paper Industry.

That the present methods for testing resistance to tearing, bursting, and tensile stresses were not considered satisfactory is evidenced by the considerable attention given to improvement of them. This is likewise true of stretch and stiffness. Further progress in measurement of surface texture as related to printing was reported.

Optical properties received their share of attention. New developments occurred in measurement of color, gloss, opacity, brightness, and in use of ultraviolet light for testing.

In the field of fiber analysis the use of fluorescent light was discussed, and new or improved methods for content of ground wood and wool, and for differentiation between bleached and unbleached fibers, were described.

The permeability of papers to fluids was given much attention. Some important developments included a more sensitive means of measurement of air permeability, and improved procedures for water-resistance.

In chemical testing, the interest in α-cellulose and copper number remained unbated, as is evidenced by the several articles mentioned. Other published material dealt with analysis of paper ash containing titanium, and determination of acidity and starch.

New ways of testing shipping containers, viscose acetate and gelatin foils, and parchment paper were described. Evidence was presented as to the validity of the heat test as an accelerated aging test. Fifty articles are cited.

Colorimetric Methods for the Determination of Phosphorus

In the Presence of Silica, Arsenic, Iron, and Nitrates

CH. ZINZADZE,[1] New Jersey Experiment Station, New Brunswick, N. J.

Two methods are outlined for the molybdimetric determination of phosphate with improvements in the preparation of the reagents leading to greater stability of the color and the elimination of the influence of silicates, arsenates, nitrates, and ferric iron.

The molybdenum blue reagent method produces the most stable color, but is slower than the reduction method using stannous chloride.

Gum arabic is offered as a protective colloid to retard the formation of turbidity which results from the use of stannous chloride.

Several other reducing agents for color development are listed.

IN PREVIOUS papers (*23*) a new molybdenum blue method for the determination of phosphorus was described differing from older methods by the use of a solution of pure molybdenum blue in sulfuric acid as reagent. (The first publication of this series was on colorimetric determination of potassium, *20*. Lewis and Marmoy, *9*, compared this method with others.) The blue color disappears upon addition to a test solution but reappears, upon heating in proportion to the amount of phosphorus pentoxide present. The blue color thus formed is stable for several days. Alten, Weiland, and Loofmann (*1*) compared this method with others and it has been employed successfully by many other investigators (*3*, *4*, *5*, *7*, *8*, *12*, *14*, *16*, *17*, *18*). Since the earlier publications, slight changes in reagent preparation and analytical procedure have been made to eliminate the influence of silicates, arsenates, nitrates, and ferric iron.

Colorless molybdenum trioxide, upon partial reduction in acid solution, yields a blue complex to which most investigators assign the formula $MoO_2.4MoO_3$. This molybdenum blue complex is extremely unstable under conditions of varying acidity, so that simple fivefold aqueous dilution of the 25 *N* sulfuric acid solution is sufficient to void the color. On the other hand, phosphoric and arsenic acids form stable blue salts—$(MoO_2.4MoO_3)_2H_3PO_4$. These blue salts may be formed (1) by the addition of molybdenum blue reagent to phosphate or arsenate solutions, (2) by the reduction of molybdenum trioxide, or (3) by the oxidation of molybdenum dioxide, in the presence of phosphate or arsenate.

1. The molybdenum blue reagent method cited above (*23*) was developed by the author and is extended in this paper together with a modification of the reduction method.
2. The reduction method was developed in 1887 by Osmond (*11*) who used stannous chloride as the reducing agent. Subsequent investigators proposed the use of other reducing agents. Bell and Doisy, Briggs and Benedict (*2*) used hydroquinone and bisulfite; Fiske and Subbarow (*6*) used aminonaphtholsulfonic acid and bisulfite; Tschopp and Tschopp (*17*) used *p*-methylaminophenol sulfate and bisulfite, etc. But most investigators (Denigès, Truog, *23*, etc.) are still using stannous chloride recommended by Osmond.
3. The oxidation method was tried first by the writer, using potassium permanganate as oxidant. It was hoped that in this case the molybdenum blue formed would be reactive enough to give the blue phosphomolybdate in the cold, but the reaction did not proceed at ordinary temperatures, and it was necessary to heat the solution. Therefore the oxidation method has no advantage over the previous two methods and was abandoned.

[1] From the University of Tiflis; Republic of Georgia (Caucasus).

The upper limit of concentration which gives a readable color by the two methods outlined should be fixed at 0.3 mg. of phosphorus pentoxide in a 50-cc. determination. The quantity of molybdenum blue necessary to give the maximum color with this amount of phosphorus pentoxide was found to be about 17.6 mg. of $MoO_2.4MoO_3$. A 20 per cent excess of molybdenum trioxide above that required for this formula was found to give somewhat better results.

Elimination of Influence of Silicates, Arsenates, Nitrates, and Ferric Iron

Silicates give with molybdenum blue the same color as phosphates. Addition of increasing quantities of sulfuric acid decreases the sensitivity of molybdenum blue to silica by repression of the ionization of the weak silicic acid to a point where it does not develop a blue color, whereas the stronger phosphoric acid remains ionized and reacts with molybdate to produce a blue color. The author found (Table I) that besides the sulfuric acid concentration the ratio of sulfuric acid to molybdenum blue is very important. Since sulfuric acid affects also the sensitivity of the reagent to phosphorus pentoxide when used in concentrations less than 0.18 *N* and more than 0.36 *N*, it was necessary to choose a ratio which would not affect the sensitivity to phosphorus pentoxide and eliminate the effect of about 150 mg. of SiO_2. The ratio of sulfuric acid to molybdenum blue equal to about 35 was found to be best.

TABLE I. INFLUENCE OF SULFURIC ACID–MOLYBDENUM BLUE RATIO (BY WEIGHT) ON SENSITIVITY TO SILICA

[Optimum quantity of molybdenum blue (17.6 mg.) is used]

Silica (SiO_2)	Sulfuric Acid–Molybdenum Blue Ratio				
Mg./50 cc.	20	25	30	35	40
0	+	−	−	−	−
50	+	+	−	−	−
100	+	+	+	−	−
150	+	+	+	+	−

\+ blue colored.
− not colored.

Sodium bisulfite was used to eliminate the influence of arsenates, nitrates, and ferric iron.

ARSENATES. Arsenic pentoxide like phosphorus pentoxide gives a blue color with molybdenum blue, but arsenic and phosphorus trioxides do not. Tschopp and Tschopp (*17*) and Tananieff and Potschinok (*15*) used sodium bisulfite for the reduction of arsenic pentoxide to trioxide. Pett (*13*) studied the influence of temperature and concentrations of sulfuric acid and sodium bisulfite on the reduction of arsenic pentoxide. The author's experiments partly confirmed the

results of Pett. It was found that at ordinary temperatures (20° to 30° C.) at least 10 hours are required for the reduction; at 50° to 100° C. it takes only one hour. In the author's experiments the upper admissible limit of concentration was found to be 20 mg. of arsenic pentoxide in 50 cc.

It is necessary to reduce arsenic pentoxide before the addition of molybdenum blue, since blue arsenomolybdate once obtained cannot be reduced by the addition of sodium bisulfite.

NITRATES. When the solution contains nitrates, the sulfuric acid of molybdenum blue solution liberates nitric acid, which oxidizes the blue phosphomolybdate, causing the color to fade. Sodium bisulfite eliminates the influence of about 50 mg. of nitric acid in 50 cc.

FERRIC IRON even in very small amounts (2 mg. of Fe_2O_3 and more) produces a greenish tint. Ferrous iron does not have such an undesirable effect. Sodium bisulfite eliminates the influence of about 50 mg. of ferric oxide in 50 cc. Upon the addition of sodium bisulfite the solution becomes red in the presence of ferric oxide but the color disappears gradually and in a few minutes the solution is clear again.

It should be emphasized that sodium bisulfite gives a blue color even in the absence of phosphorus pentoxide, unless sulfuric acid is previously added.

Description of Methods

The following reagents are used in both methods:

1. 0.1 *N* pure, carbon dioxide-free sodium (or potassium) hydroxide solution and phenolphthalein indicator.
2. 25 *N* sulfuric acid solution (C. P., A. C. S., phosphorus- and arsenic-free.)
2. 1 *N* sulfuric acid solution: 40 cc. of 25 *N* sulfuric acid diluted to 1 liter with distilled water.
4. Acid molybdic (anhydride), C. P., A. C. S., very fine powder. Extract quantity of MoO_3 in it should be known; it must be not less than 99.5 per cent. (Specify these requirements when ordering.)
5. Sodium bicarbonate solution, 2 per cent. Prepare fresh solution every month.
6. α-Dinitrophenol (2,4-dinitrophenol). Prepare a saturated aqueous solution by heating to about 50° C.; allow to stand overnight and decant the clear solution.
7. Anhydrous sodium bisulfite ($NaHSO_3$) solution, 8 per cent. This solution keeps only a week.
8. Standard phosphate solution. Dissolve 0.0767 gram of C. P. dry monobasic potassium phosphate in about 200 cc. of distilled water; add 10 cc. of 1 *N* sulfuric acid and 6 drops of 0.1 *N* potassium permanganate as preservatives; make up to exactly 2 liters. This is 20 p. p. m. of phosphorus pentoxide solution; 1 cc. = 0.02 mg. of P_2O_5. This solution keeps indefinitely in a well-stoppered Pyrex bottle, and from it the standard solutions are prepared by taking appropriate aliquots in 50-cc. volumetric flasks.

Molybdenum Blue Reagent Method

Reagents used are:

1. 0.1 *N* potassium permanganate.
2. Molybdenum metal, C. P., A. C. S. Very fine powder, containing not less than 99.5 per cent of molybdenum. (Specify these requirements when ordering.)
3. Molybdenum blue reagent (Solution I). Take, in a 3-liter Erlenmeyer flask, 1010 cc. of 25 *N* sulfuric acid; add acid molybdic (anhydride) containing exactly 40.11 grams of MoO_3; boil very gently, with occasional shaking, just until solution is complete, avoiding the evolution of white fumes; cool to room temperature; dilute with distilled water to about 998 cc., and cool again. Finally make up to exactly 1 liter with distilled water and mix well. (The solution has a bluish color.)

Solution II. Place 500 cc. of Solution I in a 3-liter Erlenmeyer flask; add 1.78 grams of molybdenum powder and boil very gently (with precautions as before) for exactly 15 minutes from incipient boiling, shaking from time to time. Allow to cool to room temperature; decant the solution from the small residue which may be present into a 500-cc. volumetric flask; dilute with distilled water to about 498 cc., and cool again. Finally make up to exactly 500 cc. with distilled water and mix well. (The solution has a greenish blue color.)

A 5-cc. aliquot of Solution II is diluted to about 50 cc. with distilled water and titrated with 0.1 *N* potassium permanganate. (It is necessary to use a pipet previously wet inside with water and washed down afterward with a few cubic centimeters of water in order to deliver 5 cc. of the viscous reagent accurately.)

The molybdenum blue reagent is finally prepared by mixing certain quantities of Solutions I and II, so that 5 cc. of the resulting mixture correspond to 5 cc. of 0.1 *N* potassium permanganate. It will keep at least 4 years, and probably indefinitely, provided it is of sufficient purity and is kept free from dust, vapors, and other contamination in a glass-stoppered Pyrex bottle.

A number of chemical houses have been selling the reagent which was suggested in a previous publication, but it was found by the author that some of the manufactured reagent samples were not pure enough and therefore did not keep long. Now several chemical houses propose to sell pure reagent with the guarantee that it will always correspond exactly to the description given here. In spite of that it is necessary to check the reagent, whether prepared in the laboratory or purchased, by making the following two tests:

1. TEST OF ACIDITY. Dilute 5 cc. of the reagent to 500 cc. and titrate 10 cc. of this diluted solution with 0.1 *N* sodium hydroxide (phenolphthalein indicator). If the reagent is exactly 25 *N*, 24.9 to 25.1 cc. of hydroxide must neutralize it.
2. TEST OF MOLYBDENUM CONCENTRATION. Titrate with 0.1 *N* potassium permanganate as indicated above; 5 cc. should oxidize an equal amount of the molybdenum blue reagent. This test must be repeated from time to time (once a month) in order to be sure that the quantity of molybdenum blue in the reagent does not change. If it changes—i. e., less than 4.9 cc. of 0.1 *N* potassium permanganate oxidizes 5 cc. of the reagent—discard the reagent.

Only 0.5 cc. of the molybdenum blue reagent is necessary for each phosphorus determination, but it is difficult to measure the reagent exactly, because of its viscosity. The difference of a few drops of the reagent can cause noticeable error, since solutions with different quantities are not comparable. It was found convenient to dilute the reagent ten times with distilled water and then to take 5 cc. of this diluted reagent for each determination. The diluted reagent does not keep more than a day.

PROCEDURE FOR DETERMINATION OF PHOSPHORUS. (In phosphate solutions containing no arsenic pentoxide, not more than about 2 mg. of ferric oxide, and about 10 mg. of nitrate, the determination of phosphorus can be made more quickly, *21*.) Take 0.5 to 15 cc. of the standard or unknown solution (containing 0.01 to 0.3 mg. of phosphorus pentoxide) in a 50-cc. volumetric flask (with a mark at 30 cc.); add 5 drops of α-dinitrophenol and neutralize drop by drop with 2 per cent sodium bicarbonate when acid, or with 1 *N* sulfuric acid when alkaline, to a very faint yellow; then add separately 5 cc. of 1 *N* sulfuric acid and 5 cc. of 8 per cent sodium bisulfite; make up to about 30 cc. with distilled water and shake well; allow to stand overnight or heat on a steam bath for at least 1 hour; add 5 cc. of ten times diluted molybdenum blue reagent, and continue to heat on the steam bath at least 30 minutes more (the velocity of color development is a function of the temperature: At 20° to 30° C. the maximum color is attained in 3 days; at 50° C. in 10 hours; at 70° C. in 3 hours; at 95° to 100° C. in 30 minutes; and by direct boiling 4 to 5 minutes); allow to cool or cool to room temperature; make up to 50 cc. with distilled water; shake thoroughly and measure the color in an ordinary or photoelectric colorimeter (*22*).

The blue color of the solutions remains stable for 2 to 3 days, provided they are stored in the dark in well-stoppered flasks. If the reagents as prepared are pure, no blue color will appear in the phosphorus-free check; it remains slightly yellowish.

It is necessary to follow exactly the directions given for unknown as well as for standard solutions, because only those determinations having the same pH reagents are comparable. For the same reason the blue color once obtained cannot be diluted.

When the color of the unknown solution is as deep as the color of standard solution containing 0.3 mg. of P_2O_5, the determination must be repeated with a smaller quantity. The difference in concentration between standard and unknown solution should not be more than 30 per cent.

The standard solutions can be used for about 2 to 3 days, but to prevent errors it is best to prepare them with each set of determinations.

Reduction Method

The principle of this method has been outlined above. If stannous chloride is used as the reducing agent, this method has the following advantages over the molybdenum blue reagent method: It does not require heating and is therefore quicker, and it is slightly more sensitive to small quantities of phosphorus pentoxide (0.005 to 0.05 mg.). However, it has a very serious disadvantage: The blue color so developed is not stable.

The following modification of the reduction method obviates the difficulties of previous investigators (*2*, *6*, *17*) by the use of pure molybdenum trioxide instead of ammonium molybdate, by the choice of the proper sulfuric acid-molybdenum blue ratio, and by careful standardization of reagent and procedure. Furthermore the influence of certain interterfering elements, such as silicates, arsenates, nitrates, and ferric iron, is eliminated and the stability of the blue color increased.

The following reagents are used:

1. Molybdenum trioxide reagent. Take, in a 500-cc. Erlenmeyer flask, 101 cc. of 25 *N* sulfuric acid; add acid molybdic (anhydride) containing exactly 4.01 grams of MoO_3; dissolve as in the preparation of Solution I of the molybdenum blue reagent; cool to room temperature; pour gradually into a 1-liter volumetric flask containing about 900 cc. of distilled water; dilute with distilled water to about 998 cc.; cool again; finally make up to exactly 1 liter with distilled water, and shake well.

To determine that the acidity is exactly 2.5 *N*, dilute 10 cc. of the reagent to 100 cc., observing the precautions for pipetting a viscous solution. Titrate 10 cc. of this diluted solution with 0.1 *N* sodium hydroxide (phenolphthalein indicator); 24.9 to 25.1 cc. of hydroxide must neutralize it.

The molybdenum trioxide reagent keeps indefinitely, provided it is kept free from dust, reducing vapor, and other contamination in a glass-stoppered Pyrex bottle.

2. Gum arabic solution. Add 10 grams of pure gum arabic (white powder, U. S. P.) to 1 liter of warm water (about 50° C.) and allow to stand for about 0.5 hour, shaking from time to time until the solution is complete. Cool to room temperature and add 1 cc. of toluene (C. P., A. C. S.) which preserves the solution for 3 to 4 weeks. Keep in a glass-stoppered Pyrex bottle. It does not matter if a precipitate forms after a few days; siphon off the clear supernatant solution for use.

Prepare a fresh solution every month.

3. Stannous chloride solution. Use fresh C. P., A. C. S., $SnCl_2.2H_2O$ preserved in well-stoppered bottles and soluble without residue. Add 0.16 gram of stannous chloride to 200 cc. of 1 per cent gum arabic solution and shake thoroughly. This solution has a slight turbidity which disappears during the determination. The solution does not keep more than about 12 hours.

Experimental Work with Stannous Chloride Solution

Stannous chloride produces maximum color in a few minutes at room temperature, but its use is accompanied by rapid fading of the blue color. To retard the formation of turbidity, the protective colloids (*10*, *19*) gum arabic, gelatin, agar-agar, soluble starch, and egg albumin were studied. Only gum arabic gave good results. Experiments showed that the optimum concentrations were: 4 mg. of stannous chloride plus 50 mg. of gum arabic for each determination. The quantity of gum arabic can be varied without any considerable effect on the determination; but any slight change in the quantity of stannous chloride has a great influence. The limits between which the optimum amounts can vary were found to be 3 to 6 mg. of stannous chloride per determination (50 cc.). The narrowness of these limits is the weakest point in the use of stannous chloride. Therefore, it is absolutely necessary to have a stannous chloride salt which corresponds as nearly as possible to $SnCl_2.2H_2O$.

The concentration of stannous chloride solution is very important. Most investigators use a few drops of concentrated solution for each determination, but the author found that slight variations in size or quantity of drops cause appreciable differences. By the use of larger volume of diluted solution, accurate measurements of the solution are assured and the results are comparable.

The addition of acid, although temporarily removing the slight initial turbidity of stannous chloride solution, accelerated its later formation and the ultimate oxidation of the salt—that is, the reducing power of the solution not containing acid lasts longer.

Procedure for Determination of Phosphorus

Prepare the aliquot for analysis as in the molybdenum blue reagent method up to the addition of the molybdenum blue reagent. If stannous chloride is used as reducing agent, allow to cool (using other reducing agents, as described below, this cooling is not necessary) or cool to room temperature (in warm solution the color fades in a few minutes), add to each flask 5 cc. of the molybdenum trioxide reagent, and mix well; prepare all standards and unknown solutions exactly in this manner; then add rapidly in turn to each flask, while shaking, 5 cc. of stannous chloride solution; make up to 50 cc. with distilled water and shake thoroughly; after 20 minutes make comparisons. The determinations should not stand longer than 6 hours; after this time the solution becomes faintly turbid.

Standards and unknowns must be prepared rapidly and simultaneously. Other precautions are the same as for the molybdenum blue reagent method.

Reducing Agents Other than Stannous Chloride

The following reducing agents may be used instead of stannous chloride:

1. *p*-Methylaminophenol sulfate, 0.4 per cent solution. Dissolve 30 grams of sodium bisulfite, anhydrous C. P., in about 200 cc. of distilled water; add 2 grams of pure dry *p*-methylaminophenol sulfate (*17*) and shake well; when dissolved make up to 500 cc.

2. Hydroquinone, 0.5 per cent solution. Dissolve 30 grams of sodium bisulfite, anhydrous C. P., and 2.5 grams of pure hydroquinone in 500 cc. of distilled water.

3. Aminonaphtholsulfonic acid, 0.05 per cent solution. Dissolve 15 grams of sodium bisulfite, anhydrous C. P., in about 100 cc. of distilled water; add 0.5 gram of dry pure 1-amino-2-naphthol-4-sulfonic acid in powdered form (*6*) and 1.5 grams of sodium sulfite, anhydrous C. P., and shake well. Warm if necessary and when dissolved make up to 500 cc.

Use 5 cc. of either and develop color at 95° to 100° C. for 30 minutes.

These reducing agents offer the advantage of greater keeping qualities (6 weeks) and stability of the blue color produced (2 days) but require heat to develop maximum color. Although more sensitive than in the original methods (*3*, *6*, *17*), color development is less rapid. At 20° to 30° C. the maximum color is attained in 5 hours, at 40° C. in 2 hours, at 60° C. in 1 hour, and 95° to 100° C. in 30 minutes.

Detection of Phosphorus with Drop Method

To a few drops of the unknown solution in a small test tube add one drop of 1 *N* sulfuric acid and one drop of 8 per cent sodium bisulfite, and boil very gently in an open flame for about 0.5 minute. After that it is possible to proceed in two different ways: Add to the boiling solution one drop of molybdenum blue reagent diluted ten times and boil another half minute, or cool it and add one drop of molybdenum oxide reagent and one drop of stannous chloride solution.

In this way it is possible to get a preliminary estimate of the approximate concentration of phosphorus in solution.

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Colorimetric Methods for Determination of Arsenic in Phosphorus-Free Solutions

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IN ANOTHER paper (*2*) citations of the use of molybdenum blue methods for the determination of phosphorus in different materials have been given. Deemer and Schricker (*1*) used this method for the determination of arsenic in plants. Slight changes and improvements which were found useful in connection with the determination of phosphorus are also applicable to the determination of arsenic.

Only pentoxides (As_2O_5 and P_2O_5) give the blue-colored compounds with molybdenum blue. Arsenic pentoxide is much more easily reduced than phosphorus pentoxide and thus it is possible to eliminate the influence of arsenic in the determination of phosphorus, but not vice versa. Consequently, the methods given in the previous paper can be used for the determination of arsenic only in solutions free from phosphorus pentoxide and containing not more than 2 mg. of ferric oxide and 10 mg. of nitrates, because sodium bisulfite reduces arsenic pentoxide and cannot be used in this determination.

These methods are particularly suitable for arsenic distillates; distillation is described in detail by Deemer and Schricker (*1*).

Reagents. With the exception of sodium bisulfite, the reagents used are exactly the same as for the determination of phosphorus (*2*).

Standard Arsenic Pentoxide Solution. Dissolve 0.0200 gram of pure anhydrous arsenic pentoxide in about 5 cc. of 2 per cent sodium bicarbonate and 100 cc. of distilled water; add 6 cc. of 1 *N* sulfuric acid and 3 drops of 0.1 *N* potassium permanganate and make up to a liter. This is 20 p. p. m. of arsenic pentoxide; 1 cc. = 0.02 mg. of As_2O_5. From this stock solution the standard solutions are prepared by taking appropriate aliquots in 50-cc. volumetric flasks.

Molybdenum Blue Reagent Method

Procedure. Pipet 0.5 to 30 cc. of the standard or unknown solution, corresponding to 0.005 to 0.3 mg. of As_2O_5, into a 50-cc. volumetric flask having a mark at 40 cc.; add 5 drops of alpha-dinitrophenol and neutralize with a 2 per cent sodium bicarbonate solution when acid, or with 1 *N* sulfuric acid when alkaline, to a faint yellow; add 5 cc. of ten times diluted molybdenum blue reagent; make up to 40 cc. with distilled water and mix; heat on a steam bath for 30 minutes; allow to cool or cool to room temperature; make up to 50 cc. with distilled water; mix well and measure the color in an ordinary or photoelectric colorimeter (*3*).

The precautions here are the same as for the determination of phosphorus.

Reduction Method

This method may be used when the molybdenum blue reagent method is inconvenient. For the determination of arsenic only stannous chloride can be used as a reducing agent; the three reducing agents mentioned in the previous paper (*2*) contain sodium bisulfite and are therefore not suitable.

Procedure. Prepare the standard or unknown as in the molybdenum blue reagent method up to the addition of the molybdenum blue reagent; add instead 5 cc. of molybdenum trioxide reagent; make up to 40 cc. with distilled water and mix; prepare all standard and unknown solutions exactly in this manner; then add rapidly in turn to each flask 5 cc. of stannous chloride solution while shaking; make up to 50 cc. with distilled water and mix thoroughly. After 20 minutes make comparisons. The determination should not stand longer than 6 hours.

Detection of Arsenic by Drop Method

To a few drops of solution add 1 drop of ten times diluted molybdenum blue reagent and boil very gently about 0.5 minute; or add one drop of molybdenum trioxide reagent and one drop of stannous chloride solution.

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Analysis of Mixtures of the Monochlorides of *n*-Pentane and Isopentane

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DURING a recent investigation of the chlorination of the pentanes, carried out in this laboratory, it was necessary to analyze mixtures of the three monochlorides of *n*-pentane and mixtures of the four monochlorides of isopentane. All the theoretically possible monochlorides derivable without carbon skeleton rearrangement are always formed upon chlorination of either normal pentane or isopentane. Polychlorides are also formed. The monochlorides can readily be separated from the polychlorides and from excess unreacted pentane by rectification. Not all the monochlorides can be separated from one another, however, by means of fractional distillation; therefore supplementary methods of analysis had to be worked out or applied. It is felt that these methods might prove applicable to other similar mixtures of aliphatic halides. They are described in this paper separately from the data obtained during the chlorination work proper.

Analysis of Mixtures of Monochlorides Derived from Isopentane

The monochlorides obtained upon chlorination of isopentane are easily separated from the polychlorides and from unchanged isopentane by fractional distillation. It is possible through repeated efficient rectification to separate the two primary chlorides as a mixture from the 2-chloro-3-methylbutane (b. p. 93.0°/760 mm.) and the 2-chloro-2-methylbutane (b. p. 85.7°/760 mm.). Separation of 1-chloro-3-methylbutane (b. p. 98.8°/760 mm.) from 1-chloro-2-methylbutane (b. p. 99.9°/760 mm.) cannot be effected with reasonable facility by fractional distillation.

The amount of 2-chloro-2-methylbutane present in the mixture of monochlorides derived from isopentane was determined by repeated hydrolysis with water at temperatures below 35° C. Whitmore and Johnston (*8*) used this method to analyze a mixture of tertiary and secondary isoamyl chlorides. The tertiary chloride undergoes hydrolysis with water at this temperature, liberating hydrochloric acid. From the amount of acid formed as determined by titration of the aqueous layer with standard alkali, the amount of tertiary amyl chloride formed was known. The secondary chloride and the two primary isoamyl chlorides are not subject to hydrolysis under these conditions.

Secondary isoamyl chloride was separated practically quantitatively from the higher boiling chlorides (isoamyl and polychlorides) by careful fractional distillation. The amount of secondary chlorides was also determined by subjecting the chloride mixture (after removal of the tertiary chloride by hydrolysis with water) to hydrolysis with 0.1 *N* silver nitrate. Whitmore and Johnston (*8*) observed that secondary isoamyl chloride is practically completely hydrolyzed in 60 hours by an excess of 0.1 *N* silver nitrate solution, whereas under the same conditions isoamyl chloride (a primary chloride) reacts only to the extent of 3 to 4 per cent.

The other primary isomer which was present—namely, 1-chloro-2-methylbutane—was shown by a special experiment to be even more resistant than isoamyl chloride to hydrolysis under these conditions. The identification of the secondary isoamyl chloride by conversion to the Grignard reagent, followed by oxygenation, hydrolysis to 3-methylbutanol-2, formation of the alpha-naphthyl urethane, and 3,5-dinitrobenzoate derivatives and taking mixed melting points with authentic samples, is described by Hass, McBee, and Weber (*3*).

After removal of the tertiary and secondary chlorides, the remaining organic chloride mixture was carefully fractionated. The fraction boiling between 98.8° and 99.9° C., representing the mixture of the two primary monochlorides of isopentane, was completely removed from the higher boiling polychlorides. This mixture of 1-chloro-3-methylbutane and 1-chloro-2-methylbutane was then analyzed according to the method described below.

Primary Monochloride Mixtures of Isopentane

The densities and refractive indices of 1-chloro-2-methylbutane and 1-chloro-3-methylbutane are not sufficiently different to serve as the basis of a method for analyzing mixtures of these two chlorides, since a mere trace of pentane or dichlorides would seriously affect the results. In synthesizing these chlorides from the corresponding alcohols it was observed that the rates of the reaction

$$C_5H_{11}OH + HCl \longrightarrow C_5H_{11}Cl + H_2O$$

differed considerably. It was suspected that the difference in reaction rates of these chlorides with potassium iodide might be sufficient to form the basis of a method of analysis.

Conant and Kirner (*2*) worked out an excellent method of determining the reaction rate constants for the reactions of a number of aliphatic halides with potassium iodide (dissolved in anhydrous acetone). With a few minor modifications their technic was used to determine the reaction rate constants of each of the two primary monochlorides of isopentane with potassium iodide (dissolved in acetone) at 60° C. Especially pure samples of these chlorides were used, prepared from the corresponding methylbutanols, which were synthesized as described below. These reaction rate constants were found to be appreciably different.

Three different known mixtures of these chlorides were prepared and their reaction rate constants with potassium iodide were determined in the same manner as those for the pure chlorides. These constants were found to be a linear function of the composition, thereby making it possible to analyze unknown mixtures with an accuracy of ±2 per cent.

Determination of Reaction Rate Constants

Test tubes 18 cm. long, made from 18-mm. Pyrex tubing, were used as the reaction vessels. A thin-walled bulb containing a known weight of the organic chloride (1-chloro-2-methylbutane or 1-chloro-3-methylbutane or a mixture of the two) was inserted into each reaction tube. Four or five small glass beads were also introduced, to aid in breaking the bulb when the reaction was to be started. Then the open end of the reaction tube was drawn down to a diameter of about 5 mm. (just large enough for a pipet to be inserted). Ten milliliters of the standard potassium iodide–acetone solution (0.04 *M* in potassium iodide) were finally introduced, and the tube was immediately sealed off.

The tubes were placed in a thermostat kept at 60° C. (±0.05°) for an hour. The reaction was started by vigorously shaking the tube, the inner bulb was thus broken, and the reactants

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were intimately mixed. At the end of a given period of time, a tube was withdrawn from the thermostat, the end broken, and the contents were quickly poured into a 250-ml. glass-stoppered, wide-mouth bottle containing a mixture of 20 grams of ice, 20 ml. of concentrated hydrochloric acid, and 5 ml. of chloroform. The bottle was immediately stoppered and shaken and the amount of potassium iodide still unreacted was determined by immediate titration with potassium iodate, according to the directions of Conant and Kirner (*2*).

Calculation of Reaction Rate Constants

The reaction $C_5H_{11}Cl + KI = C_5H_{11}I + KCl$ proceeds as a simple metathesis and, for the two primary monochlorides of isopentane, is not accompanied, under the conditions of the experiment, by any side reactions. The regular equation for bimolecular reactions

$$K_2 = \frac{1}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

was used in making the calculations for the reaction velocity constant K. The original concentration in moles per liter of the organic chloride is represented by a; b represents the original concentration of potassium iodide in moles per liter; x represents the number of moles per liter of organic chloride which reacts in t hours.

The data for the two pure chlorides and the three known mixtures are given in Table I. The average values of the reaction rate constants recorded in Table I were plotted against compositions to yield the curve shown in Figure 1. Thus, with the aid of this curve it is possible to determine the composition of any unknown mixture of the two primary monochlorides of isopentane.

Table I. Determination of Reaction Rate Constants in Metatheses between Potassium Iodide and Primary Monochlorides of Isopentane

[33.65 ml. of 0.00602 *M* potassium iodate required for 10 ml. of potassium iodide–acetone solution (blank). Thus, the latter was 0.0405 *M* in potassium iodide. Titration: ml. of 0.00602 *M* potassium iodate for unreacted potassium iodide. Composition of mixture 1: 67.4 per cent 1-chloro-3-methylbutane; mixture 2: 33.6 per cent 1-chloro-3-methylbutane; mixture 3: 49.9 per cent 1-chloro-3-methylbutane.]

Weight of Original Chloride	Potassium Iodate	Time	Reaction Velocity
Gram	*Ml.*	*Hours*	*K*
Reaction between 1-chloro-3-methylbutane and potassium iodide at 60° C.			
0.2352	17.2	21.0	0.0664
0.1797	19.1	24.0	0.0646
0.1576	18.2	30.0	0.0648
0.1619	25.0	12.0	0.0734
0.1630	14.0	43.0	0.0635
0.1514	13.3	50.0	0.0626
			Av. 0.0660
Reaction between 1-chloro-2-methylbutane and potassium iodide at 60° C.			
0.1807	30.6	20.5	0.0153
0.2071	29.5	24.0	0.0123
0.1725	27.7	45.0	0.0120
0.2033	27.9	35.0	0.0124
0.1917	24.7	58.5	0.0131
			Av. 0.0130
Reaction between mixture 1 and potassium iodide at 60° C.			
0.1644	26.1	15.5	0.0475
0.2004	21.4	23.0	0.0478
0.1527	25.0	20.0	0.0474
0.1838	16.2	40.0	0.0483
0.1668	20.6	30.0	0.0485
			Av. 0.0482
Reaction between mixture 2 and potassium iodide at 60° C.			
0.1513	22.4	42.0	0.0314
0.1436	29.0	15.5	0.0322
0.2331	22.9	25.0	0.0315
0.2127	23.0	30.0	0.0288
0.1822	26.5	20.5	0.0308
			Av. 0.0316
Reaction between mixture 3 and potassium iodide at 60° C.			
0.1851	19.0	40.0	0.0380
0.1752	26.5	16.0	0.0410
0.1773	21.6	30.0	0.0408
0.1860	23.1	25.0	0.0393
0.1872	24.8	20.5	0.0382
			Av. 0.0395

Analysis of Monochloride Mixtures of *n*-Pentane

By careful fractionation of the chlorinated products of *n*-pentane, 1-chloropentane (b. p. 108.2°/760 mm.) can be separated practically quantitatively from a mixture of 2-chloropentane (b. p. 96.7°/760 mm.) and 3-chloropentane (b. p. 97.2°/760 mm.) and from the polychlorides. This procedure was followed.

A method of analysis for the mixtures of the two secondary chlorides which did not involve separation had to be found. An effort was made to determine the reaction rate constants of these chlorides with potassium iodide, in the hope that a method of analysis similar to the one used with the mixtures of primary monochlorides of isopentane could be worked out. The results were not satisfactory because the reaction was very slow at 60° C. and the amyl iodide formed underwent considerable reduction, with formation of free iodine. The difference in the refractive indices of the two chlorides is not sufficient for analytical purposes, since a mere trace of pentane or dichlorides would seriously affect the analysis by this method. This also holds true for the densities.

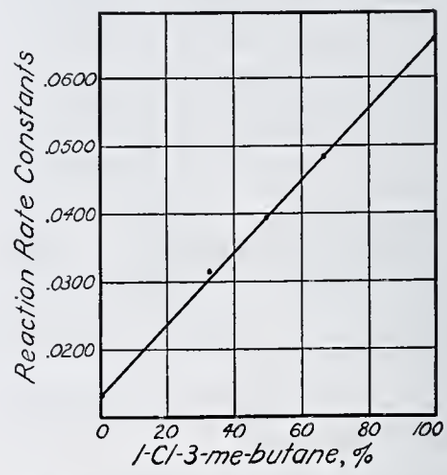

Figure 1. Diagram for Analysis of Mixtures of Primary Isoamyl Chlorides

Lauer and Stodola (*4*) developed a method of analysis for mixtures of 2-bromopentane and 3-bromopentane. After preparing the pure bromides they developed a carefully standardized procedure for the conversion of the bromides to their anilides and a large number of bromide mixtures of known composition were subjected to this procedure. The melting points of the anilide mixtures were determined and plotted against the composition of the bromides from which they were obtained. A melting point–composition diagram of the simple eutectic type was obtained which was used in analyzing unknown mixtures. This method was found to be equally applicable to the corresponding chloride mixtures and was used.

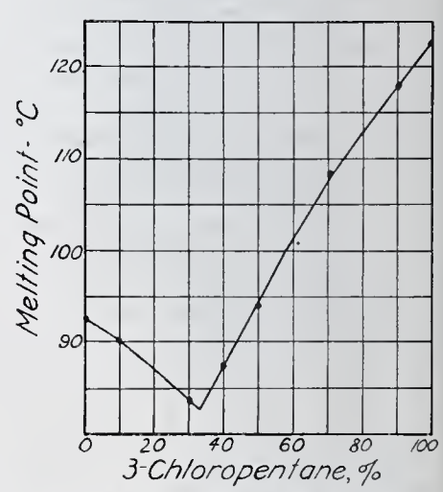

Figure 2. Diagram for Analysis of Mixtures of Secondary Chlorides of *n*-Pentane

The experimental procedure used by Lauer and Stodola for converting the bromides into the anilides was used without modification in converting the chlorides into the anilides. Six known mixtures of 2-chloropentane and 3-chloropentane were prepared and five samples of each subjected to this method of analysis. The results are contained in Table II. The diagram obtained by

plotting these average values against percentage composition is shown in Figure 2. This diagram, which checks very closely the one obtained by Lauer and Stodola on the corresponding bromopentane, was used in analyzing the unknown chloride mixtures.

Table II. Melting Points of Anilide Mixtures Obtained from Mixtures of 2-Chloropentane and 3-Chloropentane of Known Composition

	2-Chloropentane, Per Cent							
	100	90.0	69.6	59.7	50.0	29.3	9.9	0
	3-Chloropentane, Per Cent							
	0	10.0	30.4	40.3	50.0	70.7	90.0	100
	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
	92.4	89.6	82.2	87.6	94.4	107.2	117.2	122.2
	91.8	89.6	84.2	85.2	93.0	107.8	118.2	121.4
	92.8	90.2	84.6	88.6	95.2	107.5	118.5	122.4
	93.0	89.8	83.0	86.0	93.6	108.4	117.6	121.8
	92.6	90.0	82.8	87.4	94.6	108.6	117.8	122.5
	92.5	..	..	..	..	...	...	121.8
Av.	92.5	89.9	83.4	87.0	94.2	108.5	117.9	122.0

Mixtures containing more than 50 per cent of 2-chloropentane form anilide mixtures possessing melting points which represent two different percentage compositions. By observing the effect on the melting point of the mixture caused by addition of known quantities of one of the pure anilides, the exact composition was thus definitely established.

Synthesis of Amyl Chlorides

The amyl chlorides were synthesized from the corresponding alcohols. The boiling points of the two primary isoamyl alcohols differ by only 4° and the boiling points of pentanol-2 and pentanol-3 differ by less than 4°. Therefore it is practically impossible to obtain pure samples of these alcohols by fractionation of commercial products. They were synthesized by methods which could not possibly produce the other isomer of each pair.

1-Chloro-3-methylbutane. The 3-methylbutanol-1, from which this chloride was made, was synthesized from isobutyl alcohol according to the following reactions: Two kilograms of isobutyl alcohol (b. p. 107.5° to 108.0° C.) were converted into isobutyl bromide by refluxing for 10 hours with 5.6 kg. of 48 per cent hydrobromic acid and 1.7 kg. of concentrated sulfuric acid, followed by distillation at 200 mm., washing, neutralization, and rectification. Yield: 49 per cent of material of boiling point 91.0° to 91.5° C. The Grignard reagent made from this bromide was then treated with gaseous formaldehyde (generated by decomposing *p*-formaldehyde). Hydrolysis of this addition product gave 3-methylbutanol-1. After drying and rectification, a 500-gram fraction was obtained which possessed a boiling point range of 130.6° to 131.6°/760 mm. Yield: 47 per cent based on the bromide.

The 500-gram sample of this alcohol and 50 ml. of concentrated hydrochloric acid contained in a 1-liter, three-neck flask fitted with a large reflux condenser and delivery tube for hydrogen chloride, were heated to 90° C. The solution was kept saturated with hydrogen chloride at this temperature for 6 hours. The mixture was then distilled through a long column until the temperature rose to 100° C. The residual liquid was again saturated with hydrogen chloride and the above procedure repeated. After four additional treatments, about 75 per cent of the alcohol had been converted into the chloride. The combined distillates were washed with concentrated hydrochloric acid, concentrated sulfuric acid, and neutralized and dried over anhydrous potassium carbonate. Upon rectification, a 225-gram fraction of 1-chloro-3-methylbutane (b. p. 98.7° to 98.9°/760 mm.) was obtained.

1-Chloro-2-methylbutane. This was prepared from 2-methylbutanol-1, which was synthesized from butanol-2 according to the following reactions: Carefully purified butanol-2 (b. p. 99.5° to 100.0° C.) was converted into 2-bromobutane using hydrobromic and sulfuric acids as stated above with isobutyl alcohol. Yield: 53 per cent. Secondary butyl-magnesium bromide was prepared and then treated with gaseous formaldehyde. Hydrolysis of the addition product gave 2-methylbutanol (b. p. 127.5° to 127.8°/760 mm.), yield 40 per cent of theory. The procedure for converting this alcohol into the chloride was identical with the one used to prepare 1-chloro-3-methylbutane. Three hundred grams of pure 1-chloro-2-methylbutane (b. p. 99.8° to 100.0°/760 mm.) were obtained, a yield of 49 per cent based upon the alcohol.

2-Chloropentane. For the synthesis of pentanol-2, the method of Sherrill, Baldwin, and Haas was used (*6*). The alcohol boiled at 118.5° to 119.5°/760 mm. Sherrill (*7*) observed in the preparation of 3-bromopentane and 2-bromopentane from the corresponding alcohols, that if the reaction temperature be permitted to go higher than 60° C., a mixture of the two isomers was obtained instead of the individual bromide. In preparing 2-chloropentane (and also 3-chloropentane) from the corresponding alcohol, high temperatures were avoided in order to prevent, if possible, any such rearrangement during formation of the chlorides.

The pentanol-2 was saturated with hydrogen chloride at 0° C. and twice the volume of concentrated hydrochloric acid added. The resulting solution was stoppered and permitted to stand at 30° C. for 4 days. Two layers formed and the upper one was separated off. The lower layer was again saturated with hydrogen chloride and again permitted to stand at 30° C. After two additional saturations, 80 per cent of the alcohol had been converted into the chloride. The crude chloride was washed with concentrated hydrochloric acid, neutralized, and dried over anhydrous potassium carbonate. This material was rectified at 150 mm., through an efficient spiral packed column 100 cm. long and 1.5 cm. in diameter. A 300-gram fraction was collected which possessed a boiling point range of 96.6° to 96.8°/760 mm.

3-Chloropentane. The pentanol-3 from which this chloride was prepared was obtained by Grignard synthesis according to the procedure of Lucas and Moyse (*5*). Three hundred grams were obtained possessing a boiling point range of 114.8° to 115.5°/760 mm. The procedure used to convert this alcohol into the chloride is described under the preparation of 2-chloropentane. Two hundred and fifty grams of pure 3-chloropentane (b. p. 97.1° to 97.4°/760 mm.) were obtained, a yield of 69 per cent.

Summary

A new method has been developed for analyzing mixtures of two isomeric alkyl chlorides whose boiling points, refractive indices, and densities are too close to each other to serve as the basis for analytical methods. This method is based on the difference in the reaction rate constants of the alkyl chlorides with potassium iodide (dissolved in acetone).

A method of analysis for mixtures of alkyl bromides, worked out by Lauer and Stodola (*4*) is applicable to mixtures of the corresponding chlorides.

The former method should prove applicable to other similar mixtures of aliphatic chlorides. The latter method, of forming solid derivatives of the mixtures and then determining the melting points, should prove useful in a large number of analytical problems involving not only alkyl halide mixtures, but mixtures of other types of organic compounds as well.

Especially pure samples of the secondary amyl chlorides and the primary isoamyl chlorides, used in this work, were carefully synthesized and their boiling points accurately determined.

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Analytical Properties of Commercial Sulfated Alcohols

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The sodium salts of the alkyl sulfates of the type of lauryl sulfate are so similar in properties and uses to soap and to sodium salts of sulfonated fatty acids or even to sulfonated fatty glycerides that chemical distinctions must often be made. Therefore, analytical data have been obtained on three commercial grades, applying modifications of procedures commonly used in soap or sulfonated oil analysis.

The data indicate that commercial alkyl sulfates are mixtures containing mainly sodium alkyl sulfate, and substantial amounts of sodium sulfate. The instability of the product to heat renders precautions in heating vital.

Qualitatively they are identified by their instability to heat, their stability to cold acids, lathering properties when acidified, and their hydrolysis on long boiling with acid to liberate sodium bisulfate.

Quantitatively they may be estimated from the benzidine alkyl sulfate, the organic sulfate by hydrolysis, or less accurately from the loss at 110° C.

A TYPE of soaplike compound derived from the fatty alcohols by sulfation is being used in industry. Some compounded products already contain these materials and it is reasonable to expect that over a period of years their use will increase.

As yet only a limited amount of work has been done on their analytical estimation. Precipitation of the barium salt of the alkyl sulfate is unsatisfactory (*3*). The sodium alkyl sulfate cannot be quantitatively oxidized with potassium permanganate (*3*). Addition of alcohol until the solution no longer foams gives a sharp end point but is subject to many interferences (*3*).

These sodium alkyl sulfates have been estimated by titration of the alcoholic extract of their benzidine salts (*3*), but soaps, sulfated oils, and sulfonates interfere. Calculation of results according to this method requires that the nature of the alkyl group be known. Methods have also been recommended (*3*, *5*) for estimation of fatty alcohol sulfates gravimetrically as the alcohol liberated by saponification, and turbidimetrically by reaction with 1-amino-5-ethoxybenzothiazole.

The authors' purpose was to obtain data as to the behavior of the fatty alcohol sulfates in analytical procedures commonly applied to the related compounds. From these data it should be possible to outline qualitative methods for their detection and quantitative methods for their estimation in mixtures. The first of these purposes has been attained, the second only approximated.

It is to be expected that for structural reasons the alkyl sulfates will have many properties similar to those of soaps and of sulfonated oils. This would follow from the comparative structures of the compounds derived from oleic acid.

Sodium oleate:
$CH_3(CH_2)_7CH{:}CH(CH_2)_7COONa$
Sodium oleyl sulfate:
$CH_3(CH_2)_7CH{:}CH(CH_2)_7\ CH_2{-}O{-}SO_3Na$
Sodium oleyl sulfonate:
$CH_3(CH_2)_7CH_2CHSO_3Na(CH_2)_7COONa$

The most common commercial alkyl sulfates are those derived from coconut oil by hydrolysis, distillation, hydrogenation, and sulfation (*1*). The distribution of fatty acids (*4*) in coconut oil is approximately caproic 2, caprylic 9, capric 10, lauric 45, myristic 20, stearic 5, oleic 2, and palmitic 7. The extent to which these may have been segregated in commercial products, either intentionally or unintentionally is quite impossible to predict. It is probable that in the various commercial products there are varying mixtures of these acids, and that the mixtures available a few years hence will not be identical with those available now. Some of the commercial products are stated to be primarily the lauryl or the oleyl derivatives.

Materials Used

The particular materials used as a basis of this work were obtained from E. I. du Pont de Nemours & Co. It is not believed that they differ except as to proportions of ingredients from the corresponding products of other manufacturers. The grades investigated were Duponol WA concentrated, referred to as WAC; Duponol WA double concentrated, referred to as WAD, and Duponol ME dry, referred to as ME. In trade terms these are understood to be in order of increasing quality. All are dry, flaky solids.

In production it is apparently necessary to leave considerable sodium sulfate in the product. This is not unrelated to practice in the sulfonated oil industry.

Qualitative Distinctions

Given the undiluted materials, there is no difficulty in differentiating sulfonated oils, soaps, and alkyl sulfates by physical examination and a few simple tests. In solution this distinction is by no means obvious.

On acidification soaps do not lather and the liberated free fatty acid separates readily on warming. Many sulfonated oils separate in the cold on acidification, but some are moderately stable to acid and will foam on shaking after acidification in the cold. The alkyl sulfates may be acidified without resulting in separation, and the solutions still give a good lather. This is naturally related to many of the purposes for which they are used. When a sulfonated oil solution is heated with acid for a few minutes with agitation and filtered, the filtrate will give a test for sulfate. Similarly, though in a different manner, alkyl sulfate will eventually hydrolyze and sulfate may be detected. It is necessary, however, to heat the acidified solution much longer. A clear solution of alkyl sulfate and acid under this treatment gradually becomes milky-looking and finally the higher alcohol separates out on top, leaving a clear acid solution beneath, which gives a test for sulfate. These properties are so confused by the presence of sodium sulfate in both sulfonated oils and alkyl sulfate

that they require close comparison of results for even qualitative use.

Analytical Methods

Many of the analytical methods usually applied to soaps or to sulfonated oils were applied to the three grades of sodium alkyl sulfates to show similarities to and differences from soap and sulfonated oils in chemical behavior.

As a fixed point from which to work the sodium alkyl sulfates were also estimated by the benzidine method. The data, except constants on the extracts, are given in Table I. The constants on the extracts are given separately in other tables.

Loss at 110° C. Heat the samples in an open petri dish in an air oven maintained at 110° C. Reference to Table I shows that the alkyl sulfates or their decomposition products are volatile to a considerable extent at this temperature. This loss occurs over a period of at least a week, but the weight becomes constant in 9 days. The loss is greater, as would be expected, with increase of the alkyl sulfate present. This loss approximated a decomposition of sodium lauryl sulfate to give a hydrocarbon which is volatile and sodium bisulfate which remains in the residue. In the absence of other data this would appear to be a suitable method of quantitative analysis.

Table I. Analytical Data on Commerical Lauryl Sulfate

	WAC	WAD	ME
	%	%	%
Loss at 110° C.:			
6 hours	2.24	2.51	7.38
24 hours	21.28	19.49	...
9 days	31.38	45.69	53.98
Moisture by distillation	0.80	1.20	...
Ether-extractable	3.44	7.49	7.88
Alcohol-extractable	51.76	78.69	87.42
Ether-extractable from hydrolyzed solution	29.89	50.65	54.93
Organic sulfur trioxide, benzidine method	12.38	18.66	21.40
Organic sulfur trioxide, Hart-Grimshaw method	12.40	18.40	21.40
Total sulfur trioxide	36.16	29.36	25.18
Inorganic sulfur trioxide by difference	23.76	10.96	3.78
Sodium sulfate by difference	42.19	19.46	6.71
Sodium sulfate by benzidine method	43.59	20.86	7.50
Sodium chloride	1.86	1.25	1.37
Ash at 500° C.	58.34	40.70	29.83
Sodium carbonate in ash	0.16	0.16	...
Sulfur trioxide in ash	32.91	22.88	16.88
Sulfur trioxide in ash as Na_2SO_4	58.38	40.59	29.95

That this is approximately the case was confirmed by determination of sulfur trioxide in a sample which had been dried in the oven for 9 days. It showed a value of total sulfur trioxide of 38.4 as compared with 37.0 on the original sample by another method. The amount of sodium bisulfate present should be an approximate measure of the lauryl sulfate.

The loss on heating at 110° C. might be assumed to be

$$C_{12}H_{25}SO_4Na = C_{12}H_{24} + NaHSO_4$$

On that basis titration of the residue corresponds to only 19.21 per cent of sodium bisulfate present, while the loss in weight is equivalent to 26.9 per cent of sodium bisulfate. Therefore side reactions occur which lower the acidity.

The substance darkens readily in the oven, which in itself is a helpful method of distinguishing it from soap and sulfonated oils. Alkyl sulfate residues must therefore be dried on the water bath or *in vacuo*, when drying is necessary, and finished in the desiccator. Drying of residues on the water bath was used in the later determinations except where noted otherwise.

Moisture. As it is impossible to obtain this merely by heating in the oven, the xylene method was employed, adding fused potassium acid sulfate. This latter may not be necessary. No frothing whatever occurs and a very clear distillate is obtained. The results show that very little moisture is present.

Ether Extract. Extract with ether in a Soxhlet apparatus, heated on a water bath. There is some extraction for more than 8 hours. The fact that ether does not continue to extract something indicates that no substantial attack on the sodium sulfated alcohol is being obtained. This was confirmed on another sample of WAC. Extraction in 8 hours gave 3.08 per cent. Another extraction with fresh ether for 8 hours gave 0.16 per cent. A third similar extraction gave a negligible value.

Distill off the ether and heat the residue to evaporate the last of the ether on the water bath, but not longer than absolutely necessary. Small globules of oily material condense on the sides of the extraction flask. Apparently the material is slowly volatile even on a water bath. The residue after ether extraction weighed less than the original weight minus the extracted material in all three cases. This substantiates the loss by volatilization and shows that results by this method will necessarily be low. The ether extract is a yellow oil, transparent at about 30° C. and semi-solid below this. Its constants are shown in Table II.

Table II. Constants on Ether-Extractable Material from Sulfated Alcohols

	WAC	WAD	ME
Acid value	15.4	14.8	24.0
Iodine value	...	9.0	9.8

From these data and unreliable saponification values not reported it would appear that the extracts are mixtures of fatty alcohols, fatty acids, and unsaponified fat. Assuming that coconut oil had been used as starting material, representative ingredients would be dodecyl alcohol, lauric acid, and coconut oil. Lauric acid melts at 24° C. and coconut oil at 48° C. While dodecyl alcohol boils at 259° C., it is entirely probable that the vapor pressure at 100° C. would be appreciable. The existence of a saponification value greater than the acid value shows that some glyceride is present as such. The iodine values are in the range for coconut oil. Thus incomplete conversion of the fat to fatty acid and of fatty acid to fatty alcohol is indicated and will complicate analyses of commercial products containing these materials. The neutrality of the solutions of the original material and the highly acid nature of alkyl sulfuric acids are adequate evidence that such acids are absent. The extracts give no ash, indicating that the sodium alkyl sulfates are entirely insoluble in ether.

Alcohol Extract. Extract a fresh sample with alcohol in the same way as for ether extraction and for a similar period of time. Care must be observed in drying the extract. Foaming is very apt to occur and it is well to swirl the flask while the last observable amount of alcohol evaporates. Keep on the water bath only as long as necessary to remove the last traces of alcohol. Experience shows that even on the water bath the extract tends to darken. Finish drying over calcium chloride in a desiccator. Incomplete evidence indicates that the residue from drying *in vacuo* may form a compound with alcohol which is decomposed at 100° C. At any rate it tenaciously retains alcohol which is removed at 100° C.

The percentage extracts vary appreciably, depending on the amount of electrolyte present. Apparently all the sodium alcohol sulfates present are extracted by alcohol. In all cases the sum of the ether extract, alcohol extract, and sodium sulfate varies from 100 per cent.

It is very probable that the resulting extract even when carefully dried at 100° C. is not free from alcohol or is some-

what decomposed. It can only be considered as an approximation of the amount of sodium alkyl sulfate. Normally such an extract would be oven-dried, but in this case that is impossible because of instability.

Analytical data on the material extracted with alcohol are shown in Table III. The acid values as given have no significance as experience shows that they vary widely with the conditions of titration. The saponification values are not reported as they vary with the time of saponification and in several hours' heating do not remotely approach complete hydrolysis. Conditions for complete saponification could probably be developed. The small iodine values show that most of the unsaturated compounds are removed in the refining operations preceding sulfation. The sulfur trioxide content of the ash indicates that this is the sulfated alcohol fraction, as would be anticipated. However, the sulfur trioxide content of all of the alkyl sulfate is not necessarily in the ash because the alkali is not sufficient to combine with it and some may be volatilized. Results were taken on the basis of ashing without added alkali because that is a more normal commercial procedure and is the way they would be encountered in ashing of products of unknown composition. The theoretical value for sulfur trioxide in the ash if it were sodium lauryl sulfate is 13.87. This compares with values of 16.71 found for WAC, 13.18 for WAD, and 13.63 for ME. The degree of approximate indication of the amount of sodium alkyl sulfate in the low temperature ash is indicated by this method.

Table III. Constants on Alcohol-Extractable Matter from Sodium Salt of Sulfated Alcohol

	WAC	WAD	ME
Acid value	1.7	2.5	1.9
Iodine value	0.3	0.5	0.4
Ash (500° C.)	29.77	23.44	24.18
Sulfur trioxide in ash	16.71	13.18	13.62

Organic Sulfate by Benzidine Method. Add an amount of sample or sample solution to contain 0.025 to 0.5 gram of sodium alkyl sulfate to a 250-cc. flask. Dissolve in water and dilute to about 25 cc. Neutralize if necessary. Add 10 cc. of 0.05 N benzidine hydrochloride solution, or if necessary, 20 cc. Shake until the precipitate flocculates well and let stand for 10 minutes. Filter through paper and wash the flask and filter three times with 10-cc. portions of distilled water. A trace of residue adhering to the flask need not be quantitatively washed out. Wash the precipitate on the filter three times and let it drain well. Drain the water from the stem of the funnel and discard the filtrate.

Wash the precipitate on the filter with hot alcohol into the original flask until about 50 cc. of filtrate are obtained. Add 3 to 4 drops of 0.04 per cent bromocresol purple in alcohol. Heat on a water bath to slight boiling. Titrate the hot solution with 0.01 N sodium hydroxide to a yellow end point. Correct for a blank obtained by washing a similar paper with hot alcohol and similar titration to the same end point.

Calculate the titration to the sodium alkyl sulfate, using the factor corresponding to the alkyl group present or the empirical factor for the mixture present.

The inorganic sulfate was also determined by that method, starting with a new sample and omitting washing with water to avoid loss of sodium sulfate. In that case after washing the precipitate on the paper with alcohol, transfer to a flask and add 50 cc. of water. Add 5 to 6 drops of a 0.02 per cent solution of phenol red in alcohol and titrate with 0.01 N sodium hydroxide solution to a red end point.

Organic Sulfate by Hart-Grimshaw Method. The method used was that devised by Hart with modifications by Grimshaw (*2*). This method was evolved for use in the analysis of sulfonated oils, but should be of equal applicability to the alkyl sulfates.

Add 50 cc. of 0.5 N hydrochloric acid to a solution containing 2 grams of alkyl sulfate, previously exactly neutralized to methyl orange with 0.5 N hydrochloric acid. Heat in a water bath for 2 hours using a reflux condenser. The solution gradually becomes cloudy, and finally the fatty alcohol separates out on top, leaving the water layer clear. It is necessary to use a water bath. If direct heating is used, violent bumping occurs, even in the presence of glass beads. Wash down the condenser, add 30 grams of sulfate-free sodium chloride, cool, and add 20 cc. of ether to dissolve the separated alcohol. Titrate the aqueous layer with 0.5 N sodium hydroxide solution to the methyl orange end point.

The excess over the amount of standard hydrochloric acid added is due to liberated acidity from the organic sulfate group according to the following typical equation:

$$\underset{\text{Sodium lauryl sulfate}}{CH_3(CH_2)_{10}CH_2OSO_2ONa} + H_2O = \underset{\text{Lauryl alcohol}}{CH_3(CH_2)_{10}CH_2OH} + NaHSO_4$$

The hydrochloric acid acts only as a hydrolytic agent. It is clear that one equivalent of acid found by titration is equal to one molecule of sulfur trioxide.

The results, as would be expected, show increase of organic sulfate with decrease of inorganic matter present in the three samples.

It is to be expected that results by this method would be a reasonably accurate measure of the amount of sodium alkyl sulfate present. From them it should be possible to calculate a fairly accurate estimation if an average molecular weight representative of the sodium alkyl sulfate were available. This is complicated by the alkyl sulfates being mixtures so that an average value would be required for any type of product. Assuming sodium lauryl sulfate, the results obtained would give values of WAC 44.6 per cent, WAD 66.3 per cent, ME 77.1 per cent. Assuming the mixture of fatty acids normally present in coconut oil, this would give the same values, within an error negligible in this type of work.

Ether Extract after Hydrolysis. After titration in the organic sulfate determination, extract with ether 2 to 3 times and wash the combined ether extracts with water. Add this wash water to the original water layer. Evaporate off the ether on the water bath and heat exactly as in the case of the direct ether extract. This gives the liberated lauryl alcohol plus any other fatty matter that may be present. As with the organic sulfate, these values increase with decrease in inorganic content, in relatively the same order, but not in exactly the same ratio. As in the case of the ether and the alcohol extracts the drying problem reflects in a probable positive or negative error. Pedersen (*5*) has not commented on this difficulty. The constants given in Table IV are probably of little value in characterizing this extract.

Table IV. Constants on Material Extractable with Ether after Hydrolysis of Sulfated Alcohols

	WAC	WAD	ME
Iodine value	9.4	6.1	0.8
Acid value	3.0	2.4	1.4

Total Sulfate and Inorganic Sulfate. Analyze the water solution and washings from the organic sulfate determination for their sulfate content. This is the sum of that from the sodium alkyl sulfate and the sodium sulfate originally present.

A simple subtraction and calculation gives the amount of sodium sulfate in the original sample by difference. As a check on this, values for the inorganic sulfate by the benzidine method are given. Checks are satisfactory for this type of work.

Ash. Carefully ignite a 1-gram sample over a low flame, preferably slightly luminous. Do not heat at too high a temperature, as sodium sulfate melts at 884° C. and is probably somewhat volatile below that temperature. An electric muffle at about 500° C. is convenient for ashing. Analysis of this ash shows it to be almost completely sodium sulfate

and sodium chloride with a trace of sodium carbonate. The ash is greater than the sodium sulfate present as such in the original sample by an amount due to the sodium sulfate or sodium acid sulfate formed on ignition from the sodium alkyl sulfate. The same errors enter in here as in ashing the alcohol extract and preclude calculation of values for the original composition from the ash. The results are of value only as indicating the unsatisfactory nature of any results based on this figure.

Direct Titration. It is to be expected that the sodium alcohol sulfates would be salts of strong acids. This is confirmed by electrometric titration, which gives a curve typical of a salt of a strong acid.

Quantitative Methods

Having the data, it is then desirable to examine them to determine which methods can be expected to give the most satisfactory quantitative results. For convenience those found most accurate are discussed first. The data are given in Table V.

Table V. Sodium Alkyl Sulfates Present in Commercial Products

	WAC	WAD	ME
	%	%	%
Benzidine method	44.7	67.4	77.2
From organic sulfate	44.6	66.3	77.1
Loss at 110° C., less ether-extractable, over 0.583	47.9	65.5	79.1
From total extractable with ether after hydrolysis, less ether-soluble fraction originally present	40.9	66.8	72.8
Alcohol-extractable	51.76	78.69	87.42
Alcohol-extractable less ether-extractable	48.32	71.20	79.54

From the Benzidine Compound. These results have been calculated to sodium alkyl sulfate on the assumption that the alkyl part of the compound is the lauryl radical. The mixture normally derived from coconut oil would differ from this by little more than 0.5 per cent.

These values may be accepted as accurate, as a basis for comparison, since the method is concise and straightforward subject to the accuracy of the selection of the conversion factor used. The method is not applicable in the presence of soap or sulfonated oil (*3*).

From Organic Sulfate. The organic sulfate gives values which should be accurate in the presence of soap but absence of sulfonated oil. As in the benzidine method, a conversion factor is required. The fact that the results by the two methods check indicates agreement between the two methods as to the amount of sulfur trioxide present in combination with the alkyl groups. It does not validate the factor used in conversion to sodium alkyl sulfate.

From Loss at 110° C. The loss on heating at 110° C. bears a constant relation to the probable sodium alkyl sulfate content. It is purely fortuitous that division of the loss at 110° C. by 0.7 gives a value within about 1 per cent of the previous values, because the loss at 110° C. must include some or all of the ether-extractable material. Without the complication of all the figures, it can be stated that the ratio of the loss at 110° C. less the ether-extractable material to the most probable figure for the sodium alkyl sulfate content shows an average value of 0.600 with a maximum deviation of 0.027. The theoretical figure according to the assumed reaction is 0.583. This is so complicated by side reactions or otherwise as to give only an approximation. It is to be noted that the loss is higher than theoretical rather than lower. Moisture is not present for hydrolysis to lauryl alcohol and sodium bisulfate as occurs in acid solution. The method is suitable only for approximate estimation and should apply in the presence of soap and/or sulfonated oil.

From Ether Extract after Hydrolysis. Pedersen (*5*) has recommended reliance on the ether extract after hydrolysis with acid. This will be in error by the amount of ether-extractable material in the original sample due to uncombined fat, fatty acid, and unsulfated alcohol. This error would be magnified by the factor used, and, in the absence of knowledge of the distribution of the alcohols in the ether extract, an accurate factor is no more readily obtainable than for calculation from the organic sulfate. It would also be in error due to any loss in drying. Since values for the ether extract are available, this correction can be applied.

The corrected values are somewhat low for WAC and ME but in good agreement for WAD with the values by the benzidine and organic sulfate methods.

The method would not be applicable in the presence of soap or sulfonated oil without correction. Sulfonated oil would be corrected for by determination of the acetyl value of the extract. Soap would be corrected for by an acid value on the extract.

From Alcohol Extract. The alcohol extract should be a measure of the sodium alkyl sulfate. All of these results are higher than would be anticipated, even after allowing for the material extractable with ether.

Although sodium sulfate is insoluble in alcohol, it shows some solubility in an alcoholic solution of sodium alkyl sulfates. It is probable that inaccuracies in drying are a factor. However, the possibility must be considered that calculation to sodium lauryl sulfate is incorrect; that the average weight of the alkyl radical is greater than lauryl; therefore, that the factor used in calculation from the benzidine and Hart methods is inaccurate and that as a result the values for alcohol-extractable matter are nearer the true sodium alkyl sulfate values than either of the other results. The values for loss at 110° C. tend to show that this is not the case and that solubility of sodium sulfate in the alcoholic sodium alkyl sulfate solution is the source of the difference.

Conclusions

If the factor for the alkyl radical can be accurately estimated, either the Hart method or the benzidine method will give a quantitative value for total sodium alkyl sulfate.

The Hart method would be accurate even if soap were present.

An approximation from the loss at 110° C. should be obtainable even in the presence of moderate amounts of soap and/or sulfonated oil.

The ether extract after acid hydrolysis gives only a rough approximation which would require correction for soap or sulfonated oil present.

The alcohol extract gives an unduly high value for the sodium alkyl sulfate.

Much additional work must be done on commercial mixtures before final methods can be stated in full detail as applicable to sodium alkyl sulfates in various combinations.

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24 C.5

Effect of Pretreatments of Wood on the Lignin Determination

Distribution of Methoxyls in Wood

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VARIOUS treatments have been proposed (*2*, *5*, *9*) for wood previous to the lignin determination by the 72 per cent sulfuric acid method. The purpose of such pretreatments has been to reduce the likelihood of contaminating the lignin residue with decomposed extraneous materials. Pretreatments both with benzene-alcohol solution (*5*) and with alcohol-benzene solution and hot water (*9*) have been recommended for North American woods. A pretreatment with 0.5 per cent sodium hydroxide has been recommended for Australian woods (*2*). Although the three proposed pretreatments have merit for removing certain kinds of extraneous materials, they are inadequate for removing other interfering extraneous substances found in some woods. Other modifications (*6*, *7*, *10*, *11*, *12*) of the sulfuric acid method and a discussion (*4*) of the effect of the alkaline pretreatment have been published.

G. M. Kuettel of the Forest Products Laboratory has demonstrated that other troublesome extraneous materials—namely, catechol tannins—interfere with the lignin determination. The present paper proposes a modification of the sulfuric acid method, which insures the removal of catechol tannins by means of a preliminary treatment of the wood. It is recognized that the method with its proposed modification may still be inadequate for a quantitative lignin determination of some woods having unusually large percentages of still other extraneous materials.

The proposed modification is based on the fact that catechol tannins, which are incompletely soluble in the benzene-alcohol solution and hot-water pretreatments previously described for North American woods, are dissolved by pretreating the wood with 95 per cent alcohol. When analyzing wood containing no tannins the proposed pretreatment of the wood with alcohol is, of course, unnecessary; however, when analyzing woods in which the tannin content is unknown it is a safeguard.

The method recommended contains three preliminary extractive treatments of the wood. The first consists of an extraction with alcohol to remove the catechol tannins; the second, an extraction with alcohol-benzene to remove resins, oils, fats, and waxes; and the third, an extraction with hot water to remove the remaining water-soluble materials. As far as could be observed microscopically, the solid extraneous materials in the cell cavities of the unextracted wood were absent after extraction except for an occasional speck, thus indicating the removal of the visible extractives. The wood residue remaining after the three extractions is next treated with 72 per cent sulfuric acid to dissolve the cellulosic materials, leaving the lignin as a solid residue. A detailed description of the method follows.

Procedure for Determination of Lignin in Wood

Approximately 2 grams of air-dry wood in the form of sawdust (60 to 80, or 80 to 100 mesh) are weighed accurately in a tared alundum crucible. The material is then extracted for 4 hours in a Soxhlet apparatus with 95 per cent alcohol. The material is next extracted for 4 hours with alcohol-benzene solution (1 to 2 by volume). The solvent is removed by suction, the residue washed with alcohol by suction to remove the benzene and then extracted for 3 hours with 400 cc. of hot water in a hot-water bath, filtered, washed with hot water, and finally dried. The dried residue is transferred to a large glass-stoppered weighing bottle and is well mixed with 25 cc. of 72 per cent sulfuric acid at 20° C. at which temperature it is maintained for 2 hours. The resulting mixture is transferred to an Erlenmeyer flask, diluted with water to a 3 per cent acid solution, and then boiled for 4 hours under a reflux condenser. The residue is filtered on a tared alundum crucible, washed free of acid by means of hot water, dried, and weighed. The lignin content is calculated on the basis of the oven-dry unextracted sample of wood.

In case a correction for ash is desired, the lignin is transferred to a tared platinum dish and the ash content determined in the usual manner.

Test of the Method

The data obtained by the method just described were compared with those obtained according to two of the other modifications of the method previously mentioned (*5*, *9*) and also those obtained according to another modification in which alcohol is substituted for hot water for extracting the wood. Comparisons were made on the basis of (1) lignin content of the wood, (2) the methoxyl content of the isolated lignin, and (3) the percentage of the total methoxyl that is recovered in the isolated lignin. The test was made on two tannin-containing woods—redwood heartwood and white oak.

In Table I the lignin contents as determined by means of the proposed method are listed in column 2; those obtained by two previously described methods (*5*, *9*) are listed in columns 3 and 5, respectively; and those obtained by substituting hot alcohol for hot water as a pretreatment of the wood are listed in column 4.

Discussion of Results

APPARENT LIGNIN YIELDS. There is a positive increase in the apparent lignin yields in going stepwise in Table I from column 2 to column 5. In themselves they offer no explanation as to whether the differences in yields are due to an inclusion of increasing amounts of contaminants as the yields increase or to a removal of decreasing amounts of lignin as the yields increase. They are useful, however, when correlated with the data in Table II, in showing that the changes in the apparent lignin content after different extractive treatments of the wood are due to an inclusion of varying amounts of contaminants. Before it can be demonstrated that larger percentages of foreign materials are included in the higher apparent lignin yields, it is necessary to compare some characteristic chemical property of the apparent lignin residues, such as the methoxyl content.

METHOXYL CONTENT OF THE LIGNIN RESIDUES. The methoxyl content of the lignin was employed for characterizing the lignin residues, which were isolated by the four modifications of the method as indicated in the column headings of Table I. The results for comparison are recorded in Table II.

The methoxyl content determined by the Zeisel method (*1*) is highest in column 2 and successively decreases in col-

Table I. Effect of Removal of Extractives on Lignin Yields Obtained from Wood

[Percentages based on oven-dry (105° C.) weight of the unextracted wood.]

Species	Lignin in Wood Extracted with: Alcohol, alcohol-benzene, and hot water	Alcohol-benzene and hot water	Alcohol and alcohol-benzene	Alcohol-benzene only
1	2	3	4	5
Redwood (heartwood)	29.76	31.13	31.75	32.50
	30.84	31.20	31.85	32.60
	30.54	30.90	31.83	32.28
	30.77	30.96	31.56	32.06
	30.36	31.00	31.71	32.16
	30.47	31.00	...	32.28
	30.58	31.02	...	32.08
	30.32	31.02	...	32.03
	30.49	31.02	...	31.99
	30.42	...	...	...
	30.31	...	...	...
Av.	30.44	31.03	31.74	32.24
White oak	22.99	23.35	24.74	26.04
	22.56	23.50	24.87	26.14
	22.81	23.11	24.80	26.16
	22.76	23.48	24.81	26.17
	22.92	23.15	24.70	26.07
	...	...	...	25.99
Av.	22.81	23.32	24.78	26.10

Table II. Methoxyl Content of Lignin Isolated from Wood Subjected to Different Extractive Treatments

[Percentages based on the oven-dry (105° C.) weight of the isolated lignin.]

Species	Methoxyl in Lignin Isolated from Wood Extracted with: Alcohol, alcohol-benzene, and water	Alcohol-benzene and water	Alcohol, alcohol-benzene	Alcohol-benzene only
1	2	3	4	5
Redwood (heartwood)	13.61	13.44	13.43	12.68
	13.75	13.43	13.34	12.79
	13.57	13.52	13.29	12.75
Av.	13.64	13.46	13.35	12.74
White oak	20.10	19.14	18.39	17.89
	20.10	19.13	18.47	17.88
	...	...	...	17.89
Av.	20.10	19.13	18.43	17.89

umns 3, 4, and 5. These results considered in conjunction with those in the corresponding columns of Table I show that the higher methoxyl contents of the lignin residues are associated with the lower apparent lignin yields. Such data suggest the presence of larger amounts of materials having a low methoxyl content as the percentages of the apparent lignin yields increase. That such is the condition can be shown by calculating the methoxyl content of the various apparent lignin residues on a common basis as is shown in Table III. These calculated data, made on the basis of the unextracted wood, result from multiplying the methoxyl content of Table II by the content of its parent substance, the lignin, in Table I.

Inasmuch as the data in Table III are a composite of the methoxyl and the lignin yields, they therefore include any errors that might have been made during the methoxyl and the lignin determinations. A slight error in either of the procedures would account for the lowest methoxyl value for redwood lignin in column 5 of Table III. It would seem that this value should equal the others or even be slightly higher since, besides methoxyls in the lignin, it might include methoxyls associated with larger quantities of extraneous materials than are present in the other lignin residues. Allowing for slight errors in the determinations, the four values for the methoxyl content of the lignin residues from each wood are in close agreement. In other words, they are within experimental accuracy. It is therefore concluded from these results that the difference in lignin yields between columns 2, 3, 4, and 5 in Table I is due to the presence of extraneous materials having very little, if any, methoxyl. The presence of tannins in the alcohol extract of the wood was shown qualitatively by means of soluble ferric salts, indicating that at

Table III. Methoxyl Content of Lignin Isolated from Wood Subjected to Different Extractive Treatments

[Percentages based on oven-dry (105° C.) weight of the unextracted wood.]

Species	Methoxyl in Lignin Isolated from Wood Extracted with: Alcohol, alcohol-benzene, water	Alcohol-benzene, water	Alcohol, alcohol-benzene	Alcohol-benzene only
1	2	3	4	5
Redwood (heartwood)	4.15	4.17	4.23	4.10
White oak	4.58	4.46	4.56	4.67

Table IV. Distribution of Methoxyl in Wood

[Unless otherwise specified, percentages are based on the oven-dry (105° C.) weight of the unextracted wood.]

	Wood Fractions	Redwood	White Oak
1.	Methoxyl in unextracted wood	5.71	6.38
2.	Methoxyl in extracted[a] wood	4.70	5.91
3.	Methoxyl in extraneous materials (1 − 2)	1.01	0.47
4.	Methoxyl in lignin from extracted wood	4.17	4.55
5.	Methoxyl in holocellulose from extracted wood (2 − 4)	0.53	1.36
6.	Per cent of total wood methoxyl in extraneous materials (3 ÷ 1)	17.70	7.40
7.	Per cent of total wood methoxyl in lignin[b] (4 ÷ 1)	73.00	71.30
8.	Per cent of total wood methoxyl in holocellulose (5 ÷ 1)	9.30	21.30
9.	Per cent of extracted wood methoxyl in holocellulose (5 ÷ 2)	11.28[c]	23.02[c]
10.	Per cent of extracted wood methoxyl in lignin (4 ÷ 2)	88.72[c]	76.98[c]

[a] Wood was extracted consecutively with alcohol, alcohol-benzene solution, then washed with alcohol to remove benzene, and finally extracted with hot water.
[b] Lignin was isolated from wood extracted according to directions in No. 1.
[c] Calculated on the basis of the extracted wood.

least some of the tannins are removed by the proposed preliminary alcoholic treatment of the wood.

It is appropriate to mention here that in some woods methoxyl groups are associated with the extraneous materials (*3*, *13*) and the holocellulose (*8*) as well as with the lignin. The distribution of the methoxyls in these three wood fractions of redwood and white oak is shown in Table IV.

Distribution of Methoxyls in Wood. Methoxyl determinations were made on the unextracted wood; the wood extracted with alcohol, alcohol-benzene solution, and hot water; and the isolated lignin. The methoxyl content of the extraneous materials and the holocellulose was calculated by difference.

Data in lines 1, 2, and 4 of Table IV are the result of experimentation. Those in lines 3 and 5 were obtained by subtraction; those in lines 6 to 9, inclusive, by calculation. In redwood the methoxyl content of the extraneous materials is high compared with that of the corresponding result in white oak (line 3). A possibility of removing some hemicellulosic material from the wood during the pretreatment with hot water is recognized. However, until that possibility is proved an experimental fact, the data pertaining to the methoxyl content of the extraneous material and the holocellulose should remain as recorded in Table IV. Lignin and holocellulose constitute the extracted wood, as described in a previous paper (*8*). A part of the methoxyl in extracted wood is associated with the holocellulose and the remainder with the lignin (*8*). In extracted wood the percentage of the methoxyl combined with the redwood holocellulose is low compared with that combined with the white oak holocellulose (line 9); in extracted wood the percentage of the methoxyl recovered in the redwood lignin is high compared with that recovered in white oak lignin (line 10).

Summary and Conclusions

The accuracy of the determination of lignin in wood by means of the 72 per cent sulfuric acid method is affected by the amount and kind of extraneous materials incompletely removed from the wood by means of preliminary treatments.

Successive extractions of wood with 95 per cent alcohol, alcohol-benzene solution, and hot water make the 72 per cent sulfuric acid method for the lignin determination more adaptable to North American woods.

If the kind and amounts of extraneous materials present in a given species of wood are known, the preliminary treatments can be modified accordingly. For example, if catechol tannins are absent the extraction with 95 per cent alcohol may be eliminated.

The methoxyl groups of redwood and white oak woods are distributed among the extraneous materials, the holocellulose, and the lignin.

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Sampling and Analysis of Entrained Matter in Gases

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A method for the sampling and analysis of entrained matter in coke-oven gases has been devised and tested at various points during the purification of the gas. The method accounts for the following fractions of the entrained material: water, volatile organic constituents (benzene and naphthalene), benzene-soluble constituents, and constituents not soluble in benzene (coke breeze). The method is simple and the results are accurate and reproducible within about 10 per cent. The method offers a means of testing and checking the operation of scrubbers, Cottrell precipitators, and other devices for removal of entrained matter.

Many industrial gases are not "clean" at all stages of a process, but contain entrained materials which may be objectionable in further steps in the process or which may be valuable when separated from the gas. Numerous methods for the removal of this material are used, such as scrubbing and electrical precipitation, and in order to measure the efficiency of this removal, it is essential to have an accurate and reproducible means for determining the amount of entrained matter in a gas. The problem is further complicated by the complex nature of the suspended materials in many gases. This investigation was undertaken to determine the nature and quantities of such entrained matter in gases at various points at the plant of the Connecticut Coke Company in New Haven, Conn.

Various methods have been devised for the sampling and analysis of entrained matter in gases, but for the most part they have been applied to cases where the entrained matter was "dry dust," such as is found in flue gases at temperatures above the dew point. The method of Klempt (*1*), which is similar to the one used in this investigation, was used only for determination of the entrained tar and the amount of water was not measured. None of the previously described methods was applicable to a case of such complexity as that found at the Connecticut Coke Company plant. The method to be described was devised to afford a means of testing the Cottrell precipitators with respect to the removal of both entrained water and entrained tar. It is well known that such a precipitator will remove a high percentage of the total entrained matter from a gas stream, but there may be a preferential precipitation of one constituent. This proved to be the case at the Connecticut Coke Company, where the percentage of the water removed was greater than the percentage of the tar removed, indicating that raising the gas temperature so that all water would be in the form of vapor would increase the efficiency of tar removal.

Experimental

The sampling of the gas was accomplished by a filtration method similar to that given by the Research Corporation in an unpublished report. The apparatus is shown in Figure 1.

The sample tube, *A*, was of glass 20 cm. (8 inches) long and 1.6 cm. (0.625 inch) in diameter. The end was bent to a right angle and tapered slightly. The edges were ground so as to present a smooth edge to the gas stream. The filtering medium consisted of three or more plugs of glass wool, held apart by short pieces of glass tubing and packed in as tightly as possible. In use, the last plug was never discolored by tar, indicating that all entrained tar was removed by this filtering device. Some preliminary experiments were made using an extraction thimble in addition to the glass-wool filter. This proved to be unnecessary, since there was no discoloration of the thimble due to tar. Furthermore, the pressure drop, when taking a sample through the thimble, was very great and made it very difficult to obtain samples if the gas main was at a pressure less than atmospheric. The omission of the thimble simplified the apparatus considerably, which was a great advantage when it had to be carried to the tops of high towers and along elevated pipe lines. In some cases a second tube containing glass-wool plugs was included in series with the sampler. When this tube was maintained at the temperature of the main, there was no gain in weight, indicating that all entrained matter was removed in the first filter.

To obtain a sample, *A* was inserted into gas main *B* through

a special plug. A volume of gas measured by a standard wet-test meter, *C*, was sucked through the tube by the small rotary suction pump, *D*. The volume of gas taken was adjusted to give a sample weight of about 1.0 gram. The rate of sampling was such that the velocity of the gas through the sampler was equal to that in the gas stream at the point of sampling.

In the course of numerous runs in 91.5-cm. (36-inch) mains carrying coke-oven gas, it was found that the place and rate of sampling had no appreciable effect on the weight of the sample. This is clearly shown in Table I. The average velocity in the main was 8.55 meters per second.

TABLE I. EFFECT OF PLACE AND RATE OF SAMPLING OF COKE-OVEN GAS ON WEIGHT OF SAMPLE

Weight of dust, grams per cu. meter[a]	22.2	23.2	22.0	22.1	21.8
Distance from top of pipe shell, cm.	35.6	35.6	89	20	3.8
Gas velocity through tube, meters per second	9.15	5.8	9.15	5.8	9.15

[a] Gas volume reduced to 760 mm. (30 inches) Hg and 15.6° C. (60° F.).

The conclusion from this experiment was that there was sufficient turbulence in the gas stream at this point so that the suspended particles did not settle out, and that no great error was introduced if the rate of flow in the sampling tube differed somewhat from the velocity of the gas stream at the point of sampling.

The samples collected on the glass wool consisted of water and a sticky tar mass. It was believed that the tar fraction was made up of a volatile portion and a nonvolatile portion. The volatile constituents could be removed by passing dry air through the tube, and it was thought that this could be further subdivided into water, which would be absorbed by calcium chloride, and volatile tar which would be absorbed by a mineral oil. It was found, however, that benzene and toluene (which were taken as representatives of the volatile tar) were partially absorbed by the calcium chloride and only partially absorbed by a mineral oil. It was therefore decided to condense all the volatile components by means of a cold bath, and to separate them by decantation. The apparatus finally developed is shown in Figure 2.

TABLE II

Sample	Wt. of Total[a] Sample	Wt. of Water and Naphthalene	Wt. of Benzene-Soluble Tar	Wt. of Benzene-Insoluble Tar	Remarks
	Gram	*Gram*	*Gram*	*Gram*	
1	0.746	0.437	0.281	0.028	Inlet gas to scrubbers 3/6/34. Temp. 80° C.
2	0.798	0.457	0.303	0.038	
3	0.663	0.382	0.263	0.018	
Av.	0.735	0.425	0.281	0.029	
4	0.651	0.542	0.091	0.018	Exit gas from scrubbers, inlet to Cottrells 3/6/34. Temp. 30° C.
5	0.683	0.580	0.094	0.009	
Av.	0.665	0.561	0.092	0.012	
6	0.069	0.056	0.010	0.003	Exit gas from Cottrells 3/6/34. Temp. 30° C.
7	0.065	0.054	0.011	0.0004	
8	0.066	0.051	0.012	0.003	
9	0.073	0.059	0.013	0.001	
Av.	0.070	0.056	0.012	0.002	
Tar and water overflow from Cottrells, kg. per hour: obs. 444; calcd. 417					
10	0.701	0.601	0.070	0.029	Inlet gas to Cottrells 4/27/34
11	0.675	0.591	0.056	0.027	
Av.	0.688	0.597	0.063	0.028	
12	0.095	0.078	0.014	0.003	Exit gas from Cottrells 4/27/34
13	0.094	0.078	0.010	0.006	
Av.	0.094	0.078	0.012	0.004	
Tar overflow from Cottrells, kg. per hour: obs. 34.1; calcd. 53.5 Water overflow from Cottrells, kg. per hour: obs. 429; calcd. 371 Total overflow, kg. per hour: obs. 463.1; calcd. 424					
14	0.825	0.674	0.103	0.048	Inlet gas to Cottrells 5/2/34
15	0.733	0.657	0.036	0.040	Exit gas from Cottrells with no uni-directional high voltage applied to electrodes. 5/2/34
16	0.675	0.600	0.029	0.039	
17	0.667	0.600	0.029	0.038	
18	0.721	0.648	0.035	0.038	
Av.	0.697	0.626	0.032	0.039	
20	0.692	0.577	0.078	0.037	Inlet gas to Cottrell No. 1 during overload period. 5/8/34
21	0.189	0.151	0.022	0.016	Exit gas from Cottrell No. 1 during overload period. 5/8/34
22	0.166	0.132	0.022	0.012	
Av.	0.177	0.141	0.022	0.014	
23	0.632	0.549	0.053	0.030	Inlet gas to Cottrell No. 2 during overload period. 5/8/34
24	0.259	0.218	0.025	0.016	Exit gas from Cottrell No. 2 during overload period. 5/8/34
25	0.247	0.202	0.026	0.019	
Av.	0.253	0.210	0.025	0.018	

[a] All weights are given for a standard size sample of 0.0283 cu. meters (1.0 cu. ft.).

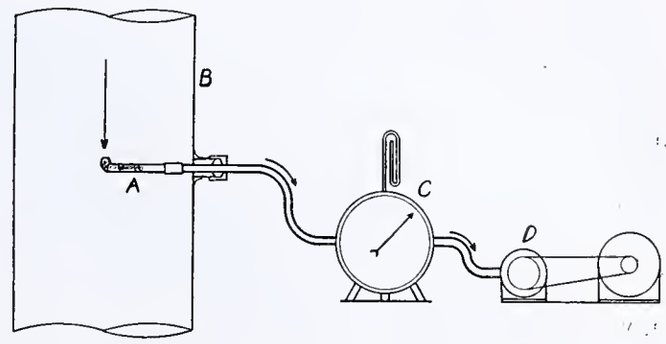

FIGURE 1. DIAGRAM OF APPARATUS FOR FILTRATION AND SAMPLING

The air, which was to be passed over the sample, was dried in a calcium chloride tower, *A*, and passed at a definite rate as measured by the flowmeter, *B*, through the sample tube, *C*, which was heated in a water bath to 95° C. The mixture of air and volatile material entered the condensing tube, *D*, through a central tube extending well toward the bottom. The condensing tube was immersed in a mixture of ice and water in a Dewar flask, *E*. With the cooling bath at 0° C. a small amount of water escaped; so a calcium chloride tube was included at *F*, and the air then passed out through the water jet pump, *G*. Experiment showed that when air was passing at a rate of 34 liters per hour (1.2 cu. ft. per hour), the passage of 11.3 liters (0.4 cu. ft.) of air was necessary to remove 1.0 gram of volatile matter and reduce the sample to a constant weight.

Some experiments were made using methanol and solid carbon dioxide as the cooling medium, but it was found that the water froze in the inlet tube of the condenser and, if the calcium chloride tube was used in connection with an ice-cooled condenser, the loss of weight of the sample was within 1 or 2 per cent of the gain in weight of the condenser and the calcium chloride tube. For convenience in cleaning, this condenser was made in two sections, closed by a ground-in joint. The lower portion of the condenser tube was graduated in cubic centimeters, so that the relative volume of oil and water layer could be read, but it was found that the volatile fraction consisted almost entirely of water with a very slight trace of naphthalene. This latter could easily be separated by extraction with ether, and evaporating this on a tared watch glass by means of a current of air.

The sample was then further separated by leaching with benzene in a modified Soxhlet extractor in which the benzene was boiled in a small flask and the vapor passed up around the sample tube and condensed by a reflux condenser, whence it passed back through the sample tube into the flask. Ten minutes was sufficient time to extract practically all the benzene-soluble material. The benzene may be evaporated and the extract weighed to check the loss in weight of the sample.

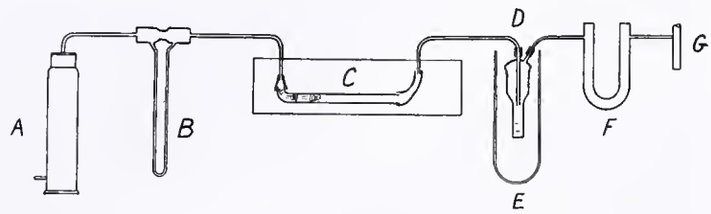

FIGURE 2. DIAGRAM OF APPARATUS FOR CONDENSATION AND SEPARATION OF VOLATILE COMPONENTS

The portion of the nonvolatile tar which is insoluble in benzene is in all probability coke breeze which was swept over from the ovens and was in all cases very small.

To summarize briefly, this method accounts for the volatile and nonvolatile portions of the suspended matter and these fractions can be further subdivided, depending on the nature and complexity of the entrained substances.

The tests summarized in Table II were made on gas passing through the primary coolers (scrubbers) and Cottrell precipi-

tators at the Connecticut Coke Company in order to get the efficiency of each unit, and inasmuch as the rate of overflow from the precipitators was known, it furnishes an excellent check on the method of sampling and analysis, and shows at once the order of reproducibility of the results.

Discussion of Results

For better understanding of the results obtained from these various tests, it is advisable to summarize briefly the operations at the Connecticut Coke Company which are directly connected with this investigation. During the process of making coke, gas containing many entrained organic compounds is evolved at a high temperature from the coke ovens. The gas is then cooled by water sprays at many points along the manifold above the ovens and consequently contains a large amount of entrained water. The gas is then sucked through the primary coolers, two scrubbers in parallel operation, whose chief function is to remove the major portion of the tar and at the same time to absorb a large portion of the ammonia from the gas. Following this scrubbing treatment, the gas is passed through two Cottrell precipitators in parallel operation whose sole purpose is to remove the last traces of suspended tar from the gas. In all subsequent steps of gas purification, it is the suspended tar and not the water which causes difficulties.

Referring to Table II, samples 1 to 13 show the "dust" content of the gas at various points during normal operation on two different days. The order of reproducibility of the results is about 10 per cent and the calculated values for the overflow from the Cottrell precipitators are of the same order. When the tar and water of the overflow were separated, the check between the observed and calculated values was not as good, because some tar was doubtless lost in evaporating off the water from the sample. Samples 14 to 18 show the effectiveness of the precipitators in removing tar when acting only as impingement surfaces, with no voltage applied to the electrodes. Samples 20 to 25 show the effect of passing all the gas through one precipitator, or, in other words, subjecting it to a 100 per cent overload.

The amount of entrained naphthalene was determined in some cases and found to be from 0.005 to 0.008 gram in the sample (0.0283 cu. meter or 1 cu. ft.) and the figures were as reproducible as other parts of the analysis.

Acknowledgment

The authors wish to acknowledge the coöperation of W. C. Wardner and B. R. Hasselman of the Connecticut Coke Company, who made it possible to obtain the data in this paper.

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RECEIVED September 25, 1934. Based on an undergraduate project of F. B. Varga.

A Rapid Method for the Determination of Sulfur in Ferromagnetic Alloys

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EXISTING methods for the determination of sulfur in iron and steel failed to give satisfactory results when applied to nickel alloys of low sulfur content. Evolution of hydrogen sulfide by solution in hydrochloric acid was inapplicable both because of the slow rate of solution of the alloy and because of the well-known fact that nickel sulfide is not readily soluble in this acid (*8*). The gravimetric method, in which the sulfur is oxidized and precipitated as barium sulfate, was found to be subject to two sources of error: (1) the tendency of iron and nickel sulfates to coprecipitate with barium sulfate, and (2) the solvent action of the relatively high concentration of hydrochloric acid in the presence of high concentrations of nickel and iron salts upon the barium sulfate. In addition to nickel and iron, many of the alloys contain molybdenum which in itself renders the gravimetric method inapplicable (*6*). This method, moreover, is very time-consuming.

Heating in hydrogen at 1100° to 1200° C., however, has provided a rapid high-precision method of determining sulfur in these alloys. The hydrogen sulfide evolved is collected in ammoniacal cadmium nitrate solution and the resulting cadmium sulfide is estimated either by the Volhard method after conversion to silver sulfide, or by a modification of the iodometric method. The method was suggested by the work of Schmitz (*9*) and other metallurgists who have shown that sulfur may be removed from nickel and iron by heating in hydrogen at high temperature. A somewhat similar method has been described by Johnson (*1*), who determined sulfur in special alloys by treatment of the sample at 1000° C. with a mixture of moist hydrogen chloride and hydrogen.

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Apparatus

A schematic diagram of the apparatus used is shown in Figure 1. A Burrell Type C-5 high-temperature furnace, fitted with a sillimanite tube tapered at one end, a purification train for the hydrogen, and an absorption flask for the collection of the hydrogen sulfide, comprise the apparatus. The absorption flask, *A*, is 27.5 cm. (11 inches) in length. The bulbs are 2.5 cm. (1 inch) and the constrictions 0.65 cm. (0.31 inch) inside diameter. The delivery tube which reaches nearly to the bottom of the absorption tube is 0.63 cm. (0.25 inch) outside diameter. The sample is held by a 12.5-cm. (5-inch) alundum boat. Hydrogen and nitrogen tanks are connected to the system by means of a three-way stopcock arrangement shown in the diagram. After displacing the oxygen in the system with nitrogen, the nitrogen is turned to waste and a properly adjusted stream of hydrogen which has been flowing to waste is simultaneously turned into the furnace.

A minimum of rubber tubing is employed in the system and the stopper used is of the "Sulfree" variety. For insertion and withdrawal of boats a nichrome wire hook is used.

Reagents

Compressed Hydrogen. The hydrogen was usually purified by passing through wash bottles containing 5 per cent silver nitrate solution and drying towers containing anhydrous calcium chloride. In one tank of hydrogen the authors found evidence of the presence of organic sulfur compounds which could only be removed by preheating at high temperature before passing

through the purification train. If the blank determination is higher than 0.002 per cent sulfur (10-gram sample basis) it is advisable to give the hydrogen the preheating treatment.

Compressed Nitrogen.

1. Volhard Method (chloride-free reagents must be employed). Standard silver nitrate solution, 0.0300 *N*, prepared and stored with the usual precautions (*2*). Sodium thiocyanate solution, approximately 0.03 *N*, prepared from the c. p. salt and standardized against pure silver or silver nitrate as described by Kolthoff and Furman (*2*). Ferric ammonium sulfate indicator, saturated solution. Ammoniacal cadmium nitrate solution, 5 per cent solution.

2. Bromate-Iodometric Method. Standard bromate-iodide solution, 0.0200 *N*: exactly 0.5567 gram of dry c. p. potassium bromate and approximately 5 grams of potassium iodide, dissolved in water, and diluted to 1 liter at 20° C. in a volumetric flask. Sodium thiosulfate solution, approximately 0.02 *N*, standardized against bromate-iodide solution immediately before use by the method recommended by Kolthoff and Furman (*3*). Starch indicator solution (*4*).

Procedure

Spread a 10-gram sample, reduced to 60-mesh filings, evenly along the bottom of a 12.5-cm. (5-inch) alundum boat. (It is not permissible to discard any portion of the sample.) Connect the tapered end of the furnace tube to the delivery tube. Place approximately 30 cc. of 5 per cent ammoniacal cadmium nitrate solution in the absorption vessel, *A*.

Allow a gentle stream of nitrogen to pass through the system for 3 minutes to expel oxygen. Open the tube and insert the boat containing sample into the hottest portion of the furnace which has already been heated to a temperature of 1100° C. Allow the stream of nitrogen to continue for 1 to 2 minutes. During this interval place the delivery tube in position in the absorption vessel. Without allowing the stream of gas to stop flowing, turn into the system a stream of hydrogen, and at the same time discontinue the nitrogen by means of the stopcock system shown in Figure 1. Continue the hydrogen for 1 hour while maintaining the temperature at 1100° to 1200° C. Do not at any time expose the cadmium sulfide to direct sunlight (*7*).

Method 1. At the end of this period disconnect the delivery tube from the furnace tube and add from a pipet 10 cc. of standard silver nitrate solution to the absorbent mixture, stirring with the delivery tube. Add 10 cc. of ammonium hydroxide and stir as before. Allow to stand for at least 20 minutes.

Filter the solution into a 400-cc. beaker, and wash precipitate with dilute (1 to 10) ammonium hydroxide solution. To the filtrate add 4 cc. of ferric alum indicator solution and then slowly add 8 *N* nitric acid until the precipitate of ferric hydroxide just dissolves. Cool to room temperature and titrate the excess silver nitrate with standard sodium thiocyanate solution according to standard practice (*2*). Use the theoretical factor.

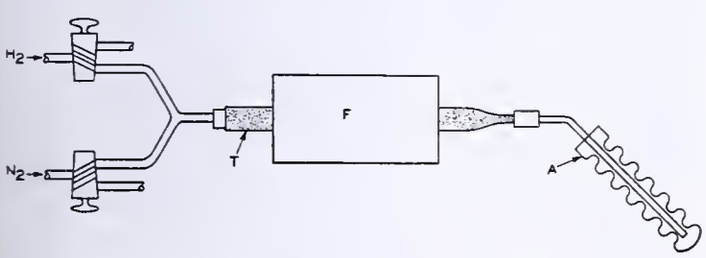

Figure 1. Schematic Diagram of Apparatus

A. Absorption tube
F. High-temperature furnace
T. Sillimanite tube

Method 2. An alternative method for estimating the sulfide collected is the following (*5*):

Transfer the absorbent solution containing cadmium sulfide to a ground-glass-stoppered iodimetric flask. Pipet 10 cc. of standard bromate-iodide solution into the absorption vessel. Acidify with hydrochloric acid (*5*) (15 cc. of concentrated hydrochloric acid to 250 cc. final volume) and transfer to the stoppered iodimetric flask, washing the absorption flask thoroughly. Add washings to flask. Stopper the flask and shake for 2 minutes. Titrate with thiosulfate solution, using starch as indicator. Use the theoretical factor.

Blank. A blank should be run on the apparatus by exactly the same procedure as used on the sample and the result deducted from the value obtained for sample.

Table I. Effect of Particle Size and Sample Size

Sample No.	Sample Weight	Mesh Size	Sulfur
	Grams		%
1	5	<60	0.0176
1	5	20–40	0.0064
2	5	<120	0.0054
2	7	<120	0.0055
2	10	<120	0.0058
3	5	<60	0.0192
3	7	<60	0.0195
3	10	<60	0.0192
Bureau of Standards No. 55 (0.017%)	10	10	0.0128

Table II. Rate of Removal of Sulfur from a High-Nickel Alloy by Heating in Hydrogen

Per Cent of Total	Time in Minutes
42.5	1
76.0	3
91.8	6
97.6	10
99.2	25
99.9	45
100.0	60
100.0	120

Table III. Precision of Method

Sample No.	Sulfur Found 1	2	3	Mean	Mean Deviation from Mean
	%	%	%	%	%
1	0.0204	0.0203	0.0203	0.0203	0.0000
2	0.0156	0.0158	0.0148	0.0154	0.0004
3	0.0142	0.0137	0.0143	0.0140	0.0003
4	0.0145	0.0108	0.0121	0.0124	0.0013
5	0.0116	0.0119	0.0120	0.0118	0.0002
6	0.0141	0.0141	0.0137	0.0139	0.0002
7	0.0141	0.0154	0.0139	0.0145	0.0005
8	0.0156	0.0185	0.0170	0.0170	0.0009
9	0.0043	0.0044	0.0044	0.0044	0.0000
10	0.0114	0.0102	0.0109	0.0108	0.0004
11	0.0111	0.0122	0.0109	0.0114	0.0005
12	0.0098	0.0120	0.0126	0.0114	0.0011
13	0.0090	0.0083	0.0094	0.0089	0.0004
14	0.0068	0.0075	0.0080	0.0076	0.0004
15	0.0100	0.0108	0.0114	0.0107	0.0005

Table IV. Comparison of Method with Acid Evolution Method

Method	No. of Determinations	Mean Sulfur Found	Mean Deviation from Mean
		%	%
Acid evolution	4	0.044	±0.002
Heating in H_2	4	0.0435	±0.0005

Experimental Data

All the data presented in this paper, except those in Table IV, were obtained by application of the Volhard method. The bromate-iodide method, however, gave results of equally high precision and is a more convenient method for routine work.

The data recorded in Table I show the influence of particle size and of sample size upon the completeness of removal of sulfur from nickel alloys by the above procedure. (No portion of the sample was discarded in any of the following experiments.)

In Table II the rate of removal of sulfur from a 10-gram sample of 60- to 80-mesh particle size is shown. These results are typical of a number of experiments.

The data presented in Table III show the precision of the method as applied to 15 typical alloys. The particle size was 60-mesh or less.

In order to compare the precision of the method with that of the standard acid evolution method (*7*), a sample of specially prepared Armco iron was analyzed by both methods. The particle size was 60-mesh or less. The results are given in Table IV.

Discussion of Results

Table I shows that the particle size of the sample must be less than 40-mesh if complete removal of the sulfur is to be achieved within 60 minutes at a temperature of 1100° C. That the removal of the sulfur from a sample is sensibly complete under the conditions recommended is indicated by the reproducibility of the method when applied to the same sample with varying sample size (Tables I and III) and by the data on the rate of removal of sulfur from a typical sample (Table II). Four samples showed in every case that the removal of the sulfur (in terms of the total removable by this method by extended treatment) was 99 per cent complete within 30 minutes. As the particle size of the sample increased the rate of removal was found to decrease. When the method was applied to Bureau of Standards Sample 55, which is approximately 10-mesh in particle size, 75 per cent of the sulfur indicated by the certificated value was recovered. This result is higher than obtained for a high-nickel alloy sample of the same mesh size, indicating the greater rate of diffusion of hydrogen in iron than in nickel.

The results presented in Table IV show that the method applied to Armco iron (to which sulfur had been added) gives results in agreement with the standard acid evolution method, provided the sample used is reduced to 60-mesh particle size.

Unfortunately, there is no direct method of obtaining data upon the accuracy of a method of this type. The reliability of the results can only be judged by (1) their reproducibility, (2) their consistency with other properties of the sample, and (3) comparison with the results obtained by other methods known to give accurate results on the samples in question. Upon the basis of these criteria the performance of the method in the authors' laboratory for the past five years indicates that no significant constant errors are involved in the method.

Summary

A method is described for the determination of sulfur in ferrous alloys of high-nickel content, wherein the sample is heated in hydrogen at 1100° to 1200° C., and the liberated hydrogen sulfide absorbed in ammoniacal cadmium nitrate solution. The method is generally applicable to iron-nickel-cobalt alloys.

The precision of the method, for the range of 0.005 to 0.020 per cent sulfur is shown to be ±0.001 per cent sulfur on the basis of a 10-gram sample.

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Sulfur Determination by the Combustion Method

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LACK of adequate methods for the separation of very small amounts of sulfur from large masses of iron, chromium, nickel, molybdenum, etc., has created an analytical problem for establishing the true quantity of sulfur present in steels. Up to the present time three methods have been used for sulfur determination: the evolution method, the hydrogen gas method, and the oxidation method. The first two deal with the separation of sulfur from iron and other alloying elements, and the third deals with the determination of sulfur in the presence of iron.

The evolution method calls for dissolving the steel in dilute hydrochloric acid and collecting the resultant gas (hydrogen sulfide) in an absorbent such as cadmium ammonium chloride. This method, though very short, does not produce accurate results because elements such as carbon, molybdenum, copper, etc., in the steel prevent the complete liberation of sulfur even in the presence of concentrated acid. This method does not function on all grades of steel, as there are many alloys insoluble in hydrochloric acid.

The hydrogen gas method calls for passing hydrogen gas over the steel in a hot tube, and collecting the resultant gas in cadmium ammonium chloride. It has no particular advantage over the evolution method except that it works with steel upon which the evolution method does not function; furthermore, the author has not found its operation very safe.

The oxidation method calls for dissolving the steels in concentrated nitric acid and precipitating the resultant compound (sulfur trioxide) with barium chloride, after replacing the nitric acid with hydrochloric acid. The results obtained by this method are dependable, although the operation is very tedious and long. Many grades of steel do not dissolve in concentrated nitric acid. By dissolving the sample in aqua regia and even in dilute nitric acid, there is a loss of sulfur which is especially pronounced on high-sulfur steels.

Observing all these difficulties, the author attempted to devise a method by which the sulfur could be separated properly from all grades of steel and ferro alloys, and the determination completed in a short time. This method is similar in many respects to the carbon determination method.

The apparatus for burning the steel is composed of a carbon furnace with a sillimanite bent-end tube, a train of gas driers such as sulfuric acid and Ascarite, and a cylinder containing a solution of sodium peroxide as absorbent. The drying train is connected to the front, and the cylinder of absorbent to the rear end of the tube. The sample is spread in a large clay boat and burned with oxygen, and the resultant sulfur dioxide and sulfur trioxide are absorbed in the sodium peroxide solution.

Procedure

Place about 1 gram of sulfur-free sodium peroxide in a glass cylinder 12.5 cm. (5 inches) tall and 2.5 cm. (1 inch) bore, add 20 to 25 cc. of distilled water, and cover tightly with a two-holed sulfur-free rubber stopper. Equip one hole with a straight glass tube, one end reaching the bottom of the cylinder and the other extending 2.5 cm. (1 inch) above the stopper. Connect this end of the glass tube to the reduced end of the combustion tube with sulfur-free rubber tubing, so that both the cylinder and the end

of the combustion tube are in intimate contact. Equip the other hole with a glass tube bent at right angles and connect this end to another cylinder containing sulfur-free sodium peroxide solution to check the overflow.

Spread 1 to 5 grams (according to sulfur content) of the steel in the furrow of alundum placed in a special clay boat (12.5 × 2.2 cm., 5 × 0.875 inch) together with 1 gram of 20-mesh metallic tin. Spread a little alundum over the sample to settle the iron dust, and introduce the boat, with a nichrome wire, to the center of the combustion tube heated to at least 1260° C. (2300° F.). Close the tube tightly with a sulfur-free one-hole rubber stopper connected to the oxygen, and permit the gas to flow in for 0.5 hour at the same speed as in the carbon determination. Shut off the oxygen gas, turn on the compressed air, and allow it to flow in at a rapid rate for 1 hour. The oxygen gas and the air are connected to the sulfuric acid bubbler with a Y-tube.

Disconnect the cylinders and transfer their contents to a 400-cc. beaker. Add 0.5 gram of sodium peroxide and boil for 5 minutes. Acidify the solution with hydrochloric acid and add 1 cc. in excess. Boil for 10 minutes, filter, and wash 4 or 5 times with hot water. The filtrate should not exceed 75 cc. in volume. Add 10 to 15 cc. of 10 per cent barium chloride solution, stir thoroughly, boil about 10 minutes to coagulate the precipitate, and allow to settle.

Add some ashless paper pulp to the beaker and stir thoroughly. Filter and wash with 1 per cent hot hydrochloric acid 4 or 5 times, and then with hot water about 10 times.

Ignite the paper holding the precipitate in a weighed platinum crucible at a dull red heat, cool, add one drop of 1 to 4 sulfuric acid and a few drops of hydrofluoric acid and evaporate until fumes are given off. Heat the crucible in a dull red muffle for 5 minutes, cool, and weigh. The gain in weight is barium sulfate.

Establish the blank on tin and other reagent by the same procedure, and deduct it from the total weight of barium sulfate. Multiply the remainder by 13.74 and divide by the number of grams of the sample used for the determination, to obtain the percentage of sulfur present in the steel.

This method has been tried on U. S. Bureau of Standards certified steel standard samples and the results are given in Table I.

Table I. Determination of Sulfur

Description	Standard Nos.	Sulfur Reported	Results of Combustion Method
		%	%
Stainless steel	73	0.031	0.033
KA2 — 18–8 steel	101	0.011	0.017
High-speed chrome tungsten vanadium	50	0.031	0.036
Chrome molybdenum	72	0.021	0.020
Nickel molybdenum	111	0.020	0.022
Chrome vanadium	30 c	0.014	0.015
Acid open hearth, 1% carbon	35 c	0.035	0.035
Acid open hearth, 1% carbon	16 b	New	0.046
Acid open hearth, 0.8% carbon	34 a	0.026	0.027
Acid open hearth, 0.4% carbon	11 c	0.026	0.028
Basic open hearth, 0.2% carbon	20 c	0.033	0.032
Iron C	5 c	0.051	0.054
Ferrochrome	64	0.070	0.076
Ferromanganese	68	0.014	0.015
Ferrosilicon	58	0.010	0.011

Comments on Literature

Several articles (*1–7*) during the last few years have discussed sulfur determination by the combustion method. In these articles the writers have suggested (1) the use of a straight combustion tube, (2) use of 1 gram of steel per determination, (3) use of sodium hydroxide for absorbent (only one writer recommends hydrogen peroxide), (4) simultaneous evolution of sulfur with carbon in 5 minutes, (5) iodine color or titration for finishing the determination, and (6) forming sulfur dioxide by the action of oxygen (*4*):

$$S + O = SO_2$$
$$SO_2 + 2I = H_2SO_4 + 2HI$$

Experiments conducted with straight combustion tubes never proved satisfactory in regard to complete evolution of sulfur in any length of time. The bent-end tube is best fitted to this work because of its shape, which prevents the deposition of sulfur trioxide vapors.

Sulfur does not leave the combustion tube simultaneously with carbon. By analyzing the absorbent every 15 minutes, the author found that the minimum time for complete generation of sulfur is 1 hour, and that two different compounds of sulfur (sulfur dioxide and sulfur trioxide) were formed. The sulfur dioxide was first generated, and there was no constant ratio between these two compounds.

Iodine in the presence of starch will titrate only sulfur dioxide absorbed in sodium hydroxide solution. According to the above reaction the formation of sulfur trioxide is entirely disregarded (*4*).

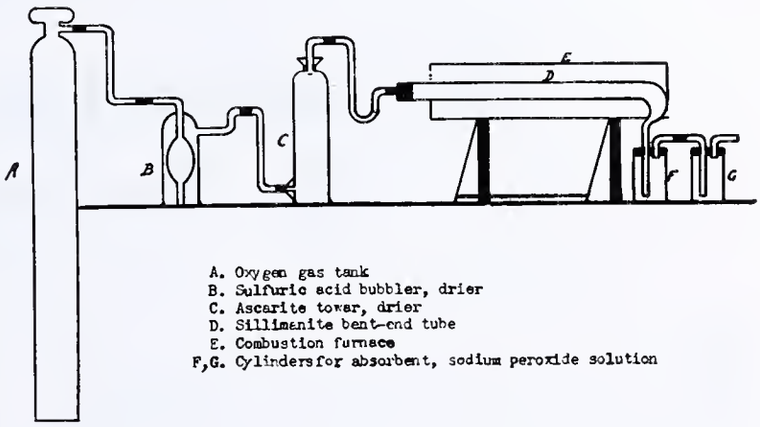

Figure 1. Apparatus for Burning Steel

Absorbing both sulfur compounds in hydrogen peroxide, boiling the solution for 10 minutes, and then titrating with standard sodium hydroxide would be satisfactory if pure hydrogen peroxide could be obtained, but all hydrogen peroxide sold on the market contains sulfuric acid.

The suggestion of using a 1-gram sample per determination confines the application of this method to certain steels, while the method described in this paper is applicable to all grades of steel, using any amount of sample (from 1 to 5 grams) according to the sulfur content of the steel.

Special Notations

The use of compressed air is suggested for economizing on oxygen gas. When combustion is complete, both the oxygen and the air have no action other than supplying a hot blast to carry out all sulfur trioxide vapors condensed within the tube.

Clay boats have been found best for this kind of work, as they do not contain sulfur, although burning them for 2 hours with oxygen before using is advisable. As metallic tin contains the least amount of sulfur, it has been chosen as flux. For pig iron and plain carbon steels the use of flux is not necessary. Clay boats must be large enough to hold 5 grams of steel; therefore, they should be made 12.5 cm. (5 inches) long and 2.2 cm. (0.875 inch) wide.

An asbestos plug need not be used in the combustion tube; it has no particular value, and contains a considerable amount of sulfur. To keep iron dust from the absorbent, the practice of spreading a little alundum over the sample is better than using an asbestos plug. Even if a little iron dust should run into the absorbent, it will not impair the result, as it will be filtered out later on. If preferred, a shield can be placed in the front end of the combustion tube to avoid the action of radiated heat, if any, on the rubber stopper.

The same sized drillings should be used in this method as for carbon determination. Use 5-gram samples if the sulfur content is less than 0.020 per cent; 4 grams for 0.020 to 0.030 per cent; 3 grams for 0.030 to 0.040 per cent; 2 grams

for 0.040 to 0.070 per cent; and 1 gram for over 0.070 per cent. Sodium hydroxide can be used for an absorbent, and when transferred to a beaker should be oxidized with either sodium peroxide or bromine water, and boiled.

This method can be put on a production basis by installing a 4- or 5-tube heavy-duty combustion furnace and working 4 or 5 samples at one time.

Keeping the bent end of the tube at nearly the same temperature as the center is important. Therefore, the ordinary furnace should be remodeled so as to keep the hump of the tube heated to the same temperature as the center (Figure 1).

When determining sulfur on ferro alloys, and especially in the case of high-carbon alloys, use 2 or 3 grams of tin and run the gas for 2 hours.

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Determination of Water in By-Product Sulfur

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THE appearance of by-product sulfur on the market (*3, 4, 6, 11*), through the adoption of liquid purification methods and sulfur-recovery processes (*7, 9, 14–16*) in the purification of manufactured, natural, and refinery gases, has necessitated proper methods of analysis. The by-product sulfur cake, if made by the ferrox process, consists essentially of water, free sulfur and iron oxide, with small quantities of sodium salts; if made by the thylox process, it consists of water, free sulfur, and a small amount of inorganic residue (sodium carbonate, sodium thiosulfates, sodium thiocyanate). The sulfur cake, as it comes from the filters, consists of a yellow-gray sticky mud containing about 60 per cent water. To handle it readily, the water content must be kept under 60 per cent. In preparing the cake at the plant, the water content has been employed as a guide as to the quality of the product made, and this requires a rapid and reliable method for the determination of water in the sulfur cake. It had been the author's practice to dry a quantity of sulfur cake in an oven at about 60° C., through which air was passed for 48 hours. This procedure was too slow for plant control purposes, and a search of the literature was made in an attempt to discover a more rapid method.

In the methods of sulfur analysis reported in the literature (*1, 8, 12*), the water or moisture content is determined by drying a known weight of material for one hour at 100° to 105° C. in an oven and calling the loss in weight water. This method could not be used for by-product sulfur cake, because of the presence of oils and organic matter that might be lost by drying at 100° to 105°, as well as the danger of loss of sulfur due to volatilization and oxidation to sulfur dioxide. With such a procedure the loss at 100° to 105° would be greater than the water content. Fresenius (*5*) and Lunge (*10*) determined the moisture content of sulfur by drying at 70° for a period no longer than necessary, but do not state how long this period may be. With these points in mind, a study was made to develop a rapid and accurate method for determining water in sulfur cake.

Experimental Work

Thirty-gram samples of by-product sulfur were dried at 100° C. in an oven through which preheated air was passed for different intervals of time. The samples were cooled in a desiccator and the percentage loss was determined. Table I presents these results, which show that there was a progressive loss of material with increase in time. What the true moisture content is cannot be ascertained from these data. (The true moisture content of the sulfur cake was 42.4 per cent, as determined by the method developed below.)

Table I. Loss When Heated at 100° C.

Time Interval	Loss by Weight
Min.	%
15	12.4
30	26.6
60	43.9
120	46.7

Loss of sulfur was found to have taken place, as indicated by the presence of sulfur crystals in the cooler portions of the exit air tube. The odor of sulfur dioxide was present in the oven, indicating that some oxidation had taken place. Any volatile oil and other products would likewise be lost. The foregoing data point out that any method for determining water in by-product sulfur cake by heating at 100° C. in an oven would be inaccurate.

In order to develop a method, some standard for reference is required. Such a standard method for water in by-product sulfur cake was developed by progressively lowering the temperature until no free sulfur was volatilized or oxidized.

Samples of sulfur cake were placed in a quart jar which was closed by a tight-fitting rubber stopper. Through glass tubes inserted in the stopper a current of dry purified air was passed over the samples. The apparatus was placed in an oven and the temperature in the jar maintained to within ±1° C. The outlet tube from the oven passed into an Erlenmeyer flask in such a manner that the air bubbled through dilute sodium hydroxide solution to remove any sulfur dioxide and volatile products that might have been driven off. All samples were dried to constant weight. Examination of the outlet tube and the sodium hydroxide solution was made for the presence of sulfur, sulfur dioxide, and oils that might be lost by volatilization or oxidation.

Starting at 100° C., the temperature was progressively lowered by 10° intervals. It was found that somewhere between 45° and 50° C. represented the highest temperature to which sulfur cake could be heated without loss of sulfur or other volatile matter. Further study within this range showed that 47° ± 2° C. was the highest temperature to which by-product sulfur cake could be heated in an oven through which dry-purified air was passed with no loss of sulfur or other volatile components. The results obtained

by drying sulfur cake at 47° ± 2°, employing the procedure outlined above, were used as a standard for reference.

The above method, while accurate, was too slow for plant control purposes; hence, the following rapid method was developed and studied. By the use of the new method, the water content of by-product sulfur cake could be determined within 3 hours, with a high degree of accuracy. The method, which was a modification and adaptation of the A. S. T. M. standard method for determining water in petroleum products (*2*), was flexible, simple, and lent itself for plant control operation.

Procedure

Figure 1 presents a diagram of the apparatus used. The procedure adopted was as follows:

Samples of by-product sulfur cake (25 grams) were weighed into the copper still, 150 ml. of gas oil and 150 ml. of rectified light oil of known moisture content were added, and the mixture was thoroughly stirred. The still was set up with the condenser and buret as shown in Figure 1. When the still was heated the water and light oil boiled over and condensed in the reflux condenser, and the water dropped to the bottom of the trap. When the trap had filled up, the excess oil ran back into the still. The heat applied to the still was so regulated that the condensed distillate fell from the end of the condenser at the rate of 2 to 5 drops per second. The ring burner was placed about 2 inches from the bottom of the still at the beginning of the distillation and gradually lowered if necessary. The boiling was continued until the meniscus in the trap remained constant for about 0.5 hour. Knowing the volume of water distilled over and the weight of a sulfur cake taken, the per cent of moisture in the sample was readily determined.

It was found that when the copper still was used daily for about 2 months with sulfur cake, it corroded through. To overcome this difficulty, the bottom section of the still was replaced by an iron part made in the author's machine shop. A number of such stills have been in almost daily use for over 3 years, and show no evidence of corrosion.

By the use of gas oil and light oil the sulfur cake was thoroughly separated, and the water had a better chance to be distilled over with the light oil. Kerosene was tried in place of the light oil, but it was not as satisfactory. The light oil and gas oil used showed the following characteristics:

	Light Oil	Gas Oil
Sp. gr. at 15.56° C.	0.865	0.839
Saybolt color	19	...

Distillation

%	° C.	%	° C.
First drop	81	First drop	204
0	75	5	242
4	90	10	253
13	95	20	268
26	100	30	279
61	120	40	288
76	135	50	299
89	155	60	311
95	176.5	70	325
96	190.5	80	341
97	200	90	362
		95	371
End point	199	End point above	371
Recovery	98		

Seil and Heiligman (*13*) developed a somewhat similar method for determining water in gas-purifying materials, employing toluene in place of gas oil and light oil. The author found that toluene was too expensive, and that the gas oil–light oil mixture decreased the time of the test somewhat.

Table II presents a comparison of the water content of by-product sulfur cake as determined by the air-drying method and the distillation method, and shows that the distillation method agrees closely with the standard air-drying method at 47° ± 2° C. The distillation method possesses a number of advantages: Once started, the determination requires no attention except an occasional reading of the trap. When the reading in the trap has been constant for about 0.5 hour, the determination is complete. The loss of sulfur by volatilization or oxidation or the loss of other volatile constituents does not enter into the determination. The water measured represents all the free water in the sample, and any side reactions that might occur on heating the sample in air are eliminated.

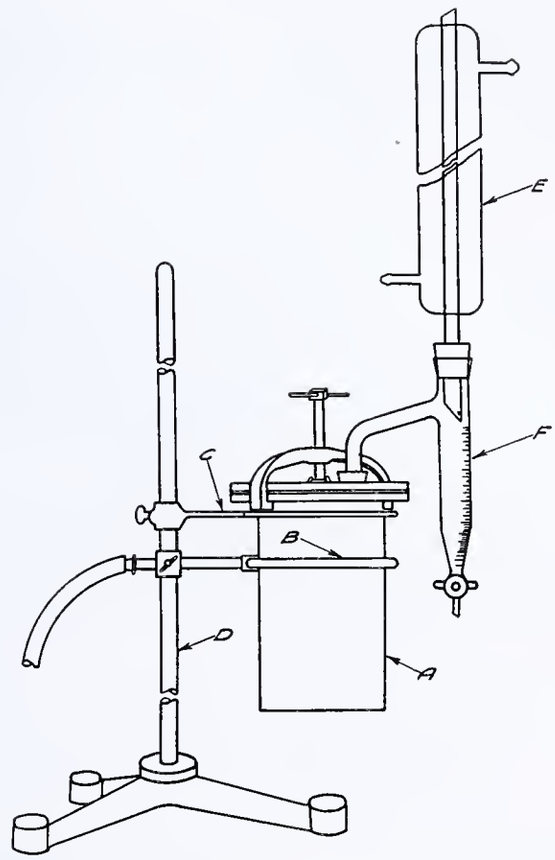

Figure 1. Diagram of Apparatus

A. Copper still, small size (No. 1260, Arthur H. Thomas Co.)
B. Ring burner (No. 1264)
C. Iron ring (No. 8761)
D. Stand (No. 9338)
E. Glass condenser, 400 mm. (No. 3901)
F. Glass trap (No. 7618-C)

Table II. Comparison of New Distillation Method with Air-Drying Method

Sample	Water Content, Per Cent by Weight: Air-drying method at 47° ± 2°	Distillation method
32024	49.4	49.2
32057	53.6	53.6
32136	48.5	48.4
32137	49.6	49.6

To prove the accuracy and reliability of the distillation method, the following experiments were conducted:

Synthetic mixtures of dried sulfur cake, water, gas oil, and rectified light oil of known moisture content were prepared and their moisture content was determined by the distillation method. Fifteen-gram samples of dried sulfur cake were treated with 17, 15, 10, 5, and 0.0 ml. of water, and then made into a paste. To this paste 150 ml. of gas oil and 150 ml. of light oil were added, with thorough mixing. The moisture content was determined by the distillation method as outlined above.

Table III. Analysis of Synthetic Water-Sulfur Mixtures

Water Added to Synthetic Mixture, Ml.	Water Determined by Distillation Method, Ml.
17.0	17.1
15.0	14.8
10.0	10.0
5.0	5.0
0.0	0.0

The data presented in Table III show that the water content of synthetic sulfur mixtures by the distillation method agreed closely with the amount of water originally added. The accuracy of the distillation method was ±0.2 ml. water. There was no interfering action between sulfur, gas oil, and light oil mixtures, upon the determination of moisture.

Summary

A rapid distillation method for the determination of water in by-product sulfur has been presented. The accuracy of the distillation method has been established from two angles—by the use of synthetic moisture-sulfur mixtures of known moisture content, and by the study of an air-drying method. Data are presented as to the accuracy of the new method. Drying the sulfur cake for 1 hour at 100° C. for moisture content gives inaccurate results.

Acknowledgment

The author wishes to acknowledge the coöperation of members of the laboratory staff, and in particular E. N. Button, Jr., in carrying out this work.

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Detection and Estimation of Orthophenylphenol

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BY VIRTUE of its relatively high phenol coefficient and other physical properties, orthophenylphenol has acquired a position of considerable importance in bacteriological investigations, and the question arose as to the possibility of detecting and estimating it if and when recovered from the body eliminations, notably the urine.

Having in mind the peculiar behavior of phenol and salicylic acid when treated with iodized potassium iodide in the presence of hot aqueous alkaline carbonates (to which one of us has already given some attention, *1–4*), it appeared not improbable that orthophenylphenol might under like circumstances develop a similar characteristic reaction. In the case of phenol and of salicylic acid (orthocarboxyphenol), the above-mentioned reagents on continued addition finally bring about the precipitation of a reddish iodine derivative, $C_6H_2I_2O$, variously designated by its earlier investigators "Lautemann's Körper," diiodophenylene oxide, tetraiodophenylene oxide, and tetraiodophenylene quinone, a substance insoluble in aqueous alkaline media and the more common organic solvents, but readily lending itself to quantitative determination.

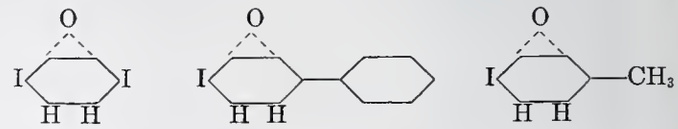
Similar tests with orthophenylphenol under conditions parallel to those observed with phenol and salicylic acid yielded immediately a characteristic purplish red precipitate, analysis of which disclosed the composition, simply expressed, $C_{12}H_7IO$, and as readily susceptible of estimation as the corresponding phenol, or salicylic acid derivative. The procedure followed is substantially that indicated below.

In a 0.5-liter Erlenmeyer flask containing a little water dissolve 200 mg. of orthophenylphenol by means of a few drops of 10 per cent sodium hydroxide solution, place on a steam bath, and add 200 ml. of distilled water, 2 grams of anhydrous sodium carbonate, and 0.2 gram of sodium bicarbonate (the latter to neutralize any free sodium hydroxide), heat for some minutes, then add 0.2 *N* iodine solution (iodized potassium iodide) in about 10-cc. portions, until after heating 15 to 20 minutes the reaction mixture retains a permanent yellow coloration, due to excess iodine. Now add just sufficient sulfur dioxide solution, if available (otherwise a small crystal of sodium sulfite), to discharge the yellow coloration, remove from bath, allow the purplish red precipitate to subside, then decant the supernatant liquid into a tared Gooch crucible, add hot water to the flask, mix thoroughly, and gradually transfer the entire precipitate quantitatively to the crucible, washing with not less than 200 ml. of hot distilled water. During the operation of washing, care should be taken that the precipitate on the filter remains somewhat moist until the final suction, otherwise cracks develop, thereby rendering a quantitative elimination of accompanying salts more difficult. After the final washing, however, the precipitate is by adequate suction almost completely freed of moisture. Finally dry in an oven at 100° C. to constant weight.

When pure, 200 mg. of orthophenylphenol should yield approximately 0.3459 gram of the iodine derivative, $C_{12}H_7IO$. In a series of controls the following recoveries were obtained: 0.3467, 0.3479, and 0.3466 gram of the iodine derivative, while determination of the iodine content (by fusion with anhydrous sodium and potassium carbonates) yielded the values 43.39 and 43.50 per cent; theoretical, 43.20 per cent. No allowance was made for traces of chlorides present, hence the relatively high percentages of iodine found.

For purposes of comparison, the corresponding iodine derivative of orthomethylphenol (orthocresol) was obtained in exactly the same manner, as a muddy light green substance, having the composition C_6H_5IO, 200 mg. of the phenol yielding 0.4270 gram of the iodine derivative; theoretical, 0.4296 gram.

For the above iodine derivatives the following structural formulas are suggested as representing their simplest molecular arrangement:



Phenol derivative — Orthophenylphenol derivative — Orthomethylphenol derivative

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Identification of Halides in the Presence of Thiocyanates

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DIFFICULTY in detecting the bromide ion in the presence of thiocyanates was reported by Curtman and Wikoff (*2*) and noted independently by the writers in student analyses. Somewhat later, Sneed and Duschak (*5*) reported the same difficulty and offered a method of destroying the thiocyanate ion by fusion of the mixture of silver halides and thiocyanate with a mixture of sodium and potassium carbonates in a platinum crucible. The hot-water solution of the melt was acidified with nitric acid, heated to boiling, and the insoluble residue of silver halides separated by filtering. The precipitate of silver halides was converted to silver sulfide by digestion with concentrated ammonium hydroxide and colorless ammonium sulfide. The presence of the halides was then determined by the successive use of ferric nitrate and nitric acid, potassium permanganate, and finally silver nitrate.

A number of difficulties have been experienced when using this method. (1) At least a partial conversion to free silver occurs during the fusion of the silver salts and the metal is not redissolved by heating the dilute nitric acid solution; consequently some of the halides are lost in the filtrate. (2) In large classes porcelain crucibles are of necessity used instead of platinum thus contaminating the sample with silicates and in some cases with chlorides.

The present work was undertaken to find a more satisfactory method of analyzing for the bromide ion in the presence of thiocyanates. Since the thiocyanate ion is oxidized to sulfuric acid and hydrocyanic acid by persulfate in acid solution (*3*), the persulfate method of determining the halides in the presence of thiocyanates as described by McAlpine and Soule (*4*) was investigated. It was soon found that no test for iodides or bromides could be obtained when as much as 5 mg. of iodide ion or 25 mg. of bromide ion was present in a sample containing 25 mg. of thiocyanate ion. The sensitiveness of the test was greatly increased by extracting a portion of the solution after the persulfate had been added but before the solution was warmed. However, the method was still regarded as inadequate.

Tests showed that the sensitivity of the test for iodides could be greatly increased by adding persulfate to a cold 10-cc. sample containing 1 to 2 cc. of carbon tetrachloride and shaking. As little as 0.25 mg. of iodide ion could be detected. That the thiocyanate ion was not destroyed during the oxidation of the iodide ion was repeatedly shown by testing a portion of the solution. However, if a sodium carbonate solution is added and the mixture is evaporated to dryness, nearly all of the thiocyanate ion will be destroyed. The small quantity remaining will be removed if the sample is slightly acidified and a small amount of persulfate is added. This last operation also serves to complete the removal of the iodide ion.

Efforts made to eliminate the evaporation to dryness of the solution were not uniformly successful. In most cases where higher concentrations of bromide ion were present satisfactory results were obtained, but the detection of small amounts of bromides in the presence of a large concentration of iodide proved very difficult, since the bromine was frequently removed with the iodine.

After the removal of the iodide ion the test for the bromide ion is made by adding carbon tetrachloride and then concentrated nitric acid. It is important in testing for small quantities of either iodide or bromide ions that the carbon tetrachloride be added before the free halogen is liberated. An orange-brown color possibly due to perthiocyanogen always appears in both the aqueous solution and the carbon tetrachloride, but disappears within a minute if the mixture in the casserole or evaporating dish is agitated. The color due to 0.5 mg. of bromine under the same conditions lasted about 5 minutes. Thus 0.5 mg. of bromide ion can be detected in the presence of 100 mg. of thiocyanate ion. The complete removal of the bromide ion is then accomplished by the addition of a slight excess of potassium permanganate and boiling one minute.

To avoid any precipitation of silver sulfate which might be mistaken for silver chloride, the sulfate ion is removed by addition of a slight excess of barium nitrate.

Procedure

TEST FOR IODIDE ION. To 10 ml. of neutral solution, add 1 ml. of carbon tetrachloride and 0.5 gram of powdered potassium persulfate in the order named and shake. A violet color indicates the iodide ion. (A minimum of 0.25 mg. of iodide ion may be detected by this method.) Shake thoroughly in a separatory funnel if available, to remove as much of the iodine from the aqueous solution as possible, and after removing the carbon tetrachloride destroy the remainder of the iodide and the thiocyanate ions, if present, before testing for the bromide ion. This is accomplished by neutralizing the solution with 2 *N* sodium carbonate and adding an additional 15 ml. of the sodium carbonate. Evaporate to dryness. A test to determine the completeness of the removal of the iodide ion should be made by dissolving the residue in 10 ml. of water, adding 1 ml. of carbon tetrachloride, acidifying with dilute nitric acid, and adding a few small crystals of potassium persulfate. Warm gently until the potassium persulfate decomposes. Unless a very large amount of iodide was present the solution will become colorless. If iodine is liberated, repeat the addition of a few crystals of potassium persulfate and the extraction until the carbon tetrachloride is no longer colored. This last step will be necessary only if a very large concentration of iodide ions was present in the original solution.

TEST FOR BROMIDE ION. When a test for an iodide is no longer obtained, add 1 ml. of carbon tetrachloride and 4 ml. of concentrated nitric acid to the cool iodide-free solution contained in a casserole or evaporating dish. The solution and the carbon tetrachloride will become orange. The mixture must be allowed to stand about a minute with occasional agitation in order to allow the orange color of the oxidation products of the thiocyanate to disappear. If as little as 0.5 mg. of bromide ion is present a yellowish color due to bromine will remain. The color of the carbon tetrachloride solution should be determined in a white casserole by daylight if possible. If desired, the solution may be transferred to a test tube and observed before a white background. If less than 0.5 mg. of bromide ion is present in 10 ml. of solution, it will be necessary to run a blank and compare the color of the carbon tetrachloride used to make the extractions.

REMOVAL OF BROMIDE ION AND TEST FOR CHLORIDE ION. The bromide ion, if present, is removed before testing for the chloride ion by adding a slight excess of potassium permanganate and boiling 1 minute. The sulfate ion formed by the decomposition of potassium persulfate must be removed by the addition of a slight excess of barium nitrate; otherwise a turbidity due to silver sulfate may form and be mistaken for a small amount of silver chloride. Filter and add silver nitrate. A curdy white precipitate proves the presence of the chloride ion.

Results

Positive tests were obtained in analyzing solutions containing the ions shown in Table I.

Table I. Solutions Giving Positive Tests

Iodide	Bromide	Chloride	Thiocyanate
Mg.	*Mg.*	*Mg.*	*Mg.*
0.25	0.25	0.25	100
0.5	0.5	0	100
0.5	2.5	0	100
0.5	100	0	100
50.0	0.5	0.5	50
50.0	0.5	0.5	0.5
100.0	100.0	15.0	100
100	100	0.25	100
100	100	100	250
100	1.0	0	0
20	0	0	100

The test for a bromide was much less sensitive in the absence of a thiocyanate. Less than 2 mg. of bromide ion could not be detected with certainty. If no bromide was present, the orange color due to the oxidation of the thiocyanate appeared but upon agitation disappeared in the course of about a minute.

Since this work was done, Curtman and Schneiderman (*1*) have published a paper, which describes a method of detecting bromides in the presence of thiocyanates, using concentrated nitric acid to oxidize the bromide ion to bromine; however, they found it necessary to destroy the thiocyanate ion by ignition of the silver salts. The smallest quantity of bromide detected in mixtures was 5 mg. (page 161), which would make the method much less sensitive than that proposed by the authors.

Summary

A method of detecting halides in a mixture containing thiocyanates has been devised, by which as little as 0.25 mg. of iodide ion, 0.5 mg. of bromide ion, and 0.25 mg. of chloride ion can be detected in the presence of 100 mg. of thiocyanate ion.

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Determination of Diphenylamine in Smokeless Powders

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The purpose of this investigation was to develop simpler and more accurate and practical methods for the determination of diphenylamine in smokeless powders.

Four methods—nitration, soda distillation, extraction, and volumetric—are given in detail. All results are based upon analyses of prepared standard samples of known composition and verified by tests on manufactured powders of known diphenylamine content.

Each method has its special application, depending on the age or condition of the powder to be tested. Excellent results were obtained with all methods.

Diphenylamine is a stabilizer introduced into smokeless powders for the purpose of retarding their decomposition. In old powders there is considerable loss of diphenylamine, some due to volatility of the diphenylamine as such, but more accounted for by nitration of the diphenylamine by the decomposition products of the nitrocellulose into nitro compounds which have no value as stabilizers (*5*). The need for accurate methods to determine the actual amount of unchanged diphenylamine left in a powder as well as the amount which was originally added to the powder led to this investigation. Practically all of this author's work is based upon Dreger's (*6*) first efforts along this line. Much work has been done by others (*1–13*).

Four methods for the determination of diphenylamine are given: (1) the nitration method, which gives the total diphenylamine originally added; (2) the soda distillation method, which gives only the active or available diphenylamine left in the powder; (3) the extraction method, which gives both the active and the inactive diphenylamine; and (4) the volumetric method, which gives the active or available diphenylamine in new powders.

Nitration for Total Diphenylamine

The literature on determining diphenylamine in smokeless powder gives the well-known nitric acid method, which is to treat the powder with about eight times its weight of concentrated nitric acid on the steam bath until the sample is all dissolved, pour the solution into water, filter off the precipitated nitro compound formed, dry, cool, and weigh. The factors for converting the weight of nitro compound to diphenylamine vary from 0.3981 to 0.4400, principally because of varying conditions which produce higher or lower yields.

The compounds formed by the nitration of pure diphenylamine by concentrated nitric acid (sp. gr. 1.42) were found to vary considerably in composition as well as yield when equal weights of diphenylamine were nitrated with equal weights of nitric acid, and any variation in the following conditions made it impossible to produce the same weight of nitro compound: concentration of acid, duration of heating, temperature of heating, and quantity of water used to precipitate the nitro compound.

The use of fuming nitric acid improved the yield considerably but it was not until pure, dry nitrocellulose was introduced that much higher yields were obtained. It was while working with reground powders in which the nitrocellulose is very finely divided that difficulty was experienced.

Table I shows results found when treating 0.05 gram of pure diphenylamine with nitric acid and mixtures of nitric acid and glacial acetic acid, the nitric acid varying from 10 to 100 per cent by volume and the acetic acid varying from 0 to 45 per cent by volume, no nitrocellulose present. All

these results are below the weight of nitro compound produced by nitrating 5 grams of a 1 per cent diphenylamine powder—which contained 0.05 gram of diphenylamine—with 10 cc. of glacial acetic and 20 cc. of concentrated nitric acid.

Table I. Results with Nitric and Acetic Acids

(No nitrocellulose, other conditions kept constant)

Test	Glacial Acetic Acid	Concd. Nitric Acid	Nitric Acid (by volume)	Nitro Compound Found
	Cc.	*Cc.*	*%*	*Gram*
1	45	5	10	0.0835
2	45	5	10	0.0822
3	40	10	20	0.0863
4	20	5	20	0.0863
5	20	10	33 1/3	0.0886
6	20	10	33 1/3	0.0837
7	15	15	50	0.0897
8	10	20	66 2/3	0.0949
9	10	20	66 2/3	0.0935
10	5	25	83 1/3	0.0920
11	0	20	100	0.0908
12	0	20	100	0.0908

Table II gives results with fuming nitric acid, all other conditions the same as in the above tests.

Table II. Results with Fuming Nitric Acid

Sample	Glacial Acetic Acid	Fuming Nitric Acid		Sulfuric Acid	Nitro Compound
	Cc.	*Cc.*	*%*	*Cc.*	*Gram*
13	10	20	66 2/3	..	0.1068
14	10	20	66 2/3	..	0.1080
15	10	10	33 1/3	10	0.1057
16	10	20	57.2	5	0.0987

These results prove that to obtain high yields, oxides of nitrogen, which are produced by nitrocellulose, must be added to give a more highly nitrating power to convert the diphenylamine completely over to hexanitrodiphenylamine, the final nitration product.

Diphenylamine Determination by Modified Nitric Acid Method

Five grams of powder, with total volatiles known, are weighed into a 250-cc. lipped beaker, 10 cc. of glacial acetic acid and 20 cc. of nitric acid (sp. gr. 1.42) are added, and the beaker is covered with a watch glass and placed on a steam bath at about 95° C. for 1.5 hours. The powder completely dissolves and diphenylamine is converted to nitrodiphenylamine. Red fumes are copiously evolved. The time and temperature stated will allow all red fumes to be dissipated without too much reduction in volume and this is the end to be attained, as the nitro compounds have a tendency to crystallize out if the solution is evaporated too much or is allowed to stand too long after removal from steam bath. Whenever such crystallization occurs results are slightly low.

Immediately after the heating on the steam bath is completed, the solution is cooled, being careful not to agitate it, and poured into 75 cc. of distilled water which has been cooled to 15° C. in a 250-cc. glass-stoppered Erlenmeyer flask. The beaker is washed with water, so that the solution including washings will be approximately 120 cc. The flask is shaken well for about 2 minutes and allowed to stand 2 hours.

The nitro compound is filtered on a Gooch crucible prepared by washing with 10 per cent nitric acid and igniting. The nitro compound is washed 6 or 7 times with water containing 1 per cent nitric acid and dried at 100° to 105° C. for 1 hour. After weighing, the Gooch is placed in a small beaker and 10 cc. of acetone are added and allowed to soak 15 minutes. The Gooch is then placed in a suction flask and washed with small quantities of acetone until nitro compounds are completely washed out. The Gooch is dried at 100° to 105° C. for 1 hour and nitro compounds are determined by loss of weight.

The factor for conversion of nitro compounds to diphenylamine, using the quantities of acid stated above, is 0.4259.

$$\text{Per cent of diphenylamine} = \frac{\text{weight of nitro compound} \times 0.4259 \times 100}{\text{weight of powder less total volatiles}}$$

Method for Establishing Factor. A weighed quantity of dry diphenylamine (0.05 gram) is transferred to a 250-cc. lipped beaker and 10 cc. of glacial acetic acid are added, stirred, and allowed to stand until all is in solution; 5 grams of dry nitrocellulose are then added and the acetic acid is mixed with nitrocellulose until it is as much colloided as this quantity of acetic acid will allow. Twenty cubic centimeters of nitric acid (sp. gr. 1.42) are added by washing down the sides of the beaker, so that all nitrocellulose will be in contact with the acid. The beaker is then covered with a watch glass and placed on the steam bath at about 95° C. for 1.5 hours. The procedure from this point is identical with that when diphenylamine is determined in powder.

Experiments. A test of diphenylamine in a sample, No. 6, containing 2.65 per cent of total volatiles, was made, using various quantities of nitric acid and the factor corresponding to the particular quantity of nitric used, with all other details constant as above.

Nitric acid, cc.	20	30	50
Weight of nitro compound, gram	0.1100	0.1092	0.1072
	0.1100	0.1097	0.1077
Factor	0.4259	0.4295	0.4333
Diphenylamine, per cent	0.96	0.96	0.956

A comparison of the straight nitric acid method without acetic using the same technic as to time, temperature, etc., and the same sample, No. 6, with 30 cc. of nitric acid, gave:

Weight of nitro compounds, gram	0.1084, 0.1090, 0.1094, 0.1097, 0.1107
Av.	0.1092
Factor	0.4295
Diphenylamine, per cent	
Max.	0.977
Min.	0.956
Av.	0.963

Experiments indicate that the factor 0.4259 is sufficiently close to use with commercial diphenylamine containing 0.097 per cent of water:

Diphenylamine (commercial), gram	0.05
Nitrocellulose, grams	5
Acetic acid, cc.	10
Nitric acid, cc.	20
Water, cc.	75
Weight of nitro compounds, gram	0.1176, 0.1178, 0.1175

Determining factors with pure diphenylamine and varying the amount of diphenylamine taken and quantities of acetic acid, nitric acid, and water used to precipitate, when the time of heating and temperature are kept constant, Table III gives a compilation of results. From the standpoint of speed, accuracy, and practicability of method the mixture of 2 parts of nitric acid and 1 part of glacial acetic acid proved the best. Where higher yields were obtained the time of solution was too long.

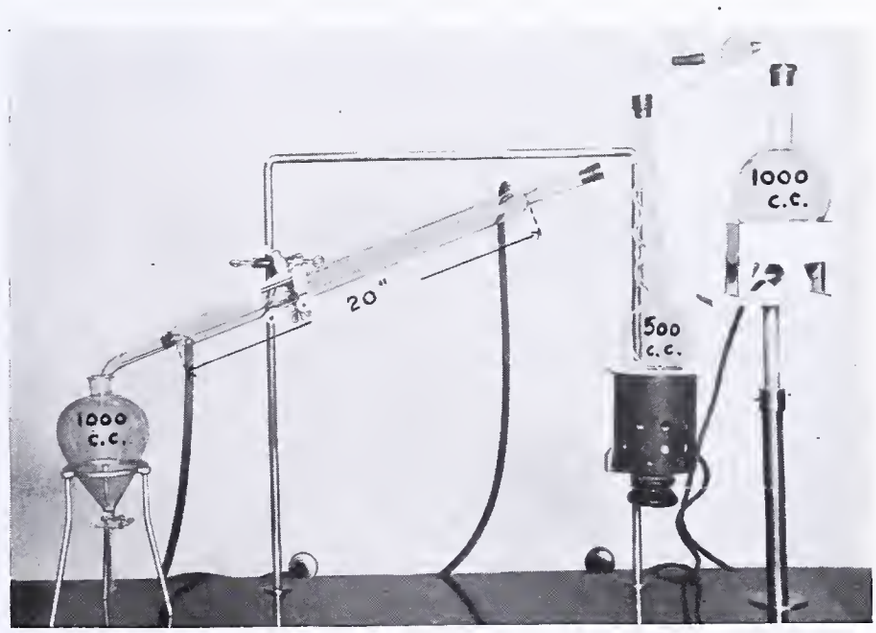

Figure 1. Apparatus for Determination of Diphenylamine by Distillation Method

The acetic acid modification is a distinct improvement in controlling the speed of reaction and allows closer checking on repeated tests than the straight nitric method, especially when reground powders are tested. The distinct increase in weight of nitro compounds, as the amount of nitric acid is reduced, may be due to solubility of the nitro compounds.

Nitration of Nitrodiphenylamines

To determine, individually, the action of nitration on diphenylamine and the various nitrated products of diphenylamine, such as are produced in the natural aging of the powder, various weights of these compounds were taken, each weight being equivalent to 0.05 gram of diphenylamine, and the following were added: 5 grams of dry nitrocellulose, 10 cc. glacial acetic acid, and 20 cc. of concentrated nitric acid. This was run for 1.5 hours on the steam bath, and the determination carried out exactly as described above. The weight of nitro compound formed in each case was about 0.1160 gram. Using the factor of 0.4259 for converting to diphenylamine, the yields were almost 100 per cent, a very good indication that each one of these compounds nitrated to the same final nitration product—hexanitrodiphenylamine (Table IV).

Table III. Determination of Factor

Diphenylamine	Nitrocellulose	Acetic Acid	Water	Nitric Acid	Nitro Compound	Factor Av.
Gram	*Grams*	*Cc.*	*Cc.*	*Cc.*	*Gram*	
0.025	5	10	75	10	0.0633, 0.0643, ...	0.3920
				20	0.0611, 0.0611, 0.0610	0.4091
				30	0.0605, 0.0600, 0.0605	0.4145
				..	0.0603, 0.0605, ...	....
				50	0.0601, 0.0590, 0.0593	0.4181
0.05	5	10	75	10	0.1200, 0.1200, 0.1210	0.4149
				20	0.1174, 0.1175, 0.1174	0.4259
				30	0.1170, 0.1161, 0.1160	0.4297
0.05	5	15	75	20	0.1186, 0.1184, ...	0.4219
		20	75	20	0.1167, 0.1178, ...	0.4266
		10	125	20	0.1183, 0.1185, 0.1177	0.4229
0.075	5	10	75	10	0.1760, 0.1780, ...	0.4237
				20	0.1747, 0.1744, ...	0.4293
				30	0.1746, 0.1747, 0.1746	....
				..	0.1749, 0.1746, 0.1747	0.4293
				50	0.1695, 0.1690, ...	0.4430
0.075	5	10	125	50	0.1676, 0.1678, ...	0.4472
0.10	5	10	75	20	0.2319, 0.2314, 0.2322	0.4314
				30	0.2293, 0.2274, 0.2276	0.4385

Table IV. Nitration of Diphenylamine and Its Nitrated Products

(Using 5 grams of dry nitrocellulose with 10 cc. of glacial acetic acid and 20 cc. of concentrated nitric acid 1.5 hours on steam bath)

Compounds Taken for Nitration	Actual Weight Taken	Equivalent Diphenylamine	Nitro Compound Found	Yield as Diphenylamine[a]
	Gram	*Gram*	*Gram*	%
Diphenylamine, m. p. 52.5° C.	0.0500	0.05	0.1169	99.57
			0.1176	100.00
Diphenylnitrosamine, m. p. 66.0° C.	0.0585	0.05	0.1159	98.72
Nitrodiphenylnitrosamine, m. p. 130° C.	0.0719	0.05	0.1168	99.49
Dinitrodiphenylamine, m. p. 156.5° C.	0.0766	0.05	0.1157	98.55
Trinitrodiphenylamine, m. p. 181.0° C.	0.0930	0.05	0.1150	98.20

[a] Factor 0.4259 used for conversion.

To verify this by melting point, small amounts of the yellow nitro compound were placed on the surface of mercury contained in a large porcelain crucible in which was supported a thermometer. Melting points gave 239° to 242° C. Beilstein (*1*) and Marshall (*11*) give 238° C. as the melting point for 2, 4, 6, 2′, 4′, 6′-hexanitrodiphenylamine, the symmetrical form. When using a regular melting point tube for the test, the compound seems to decompose slowly and reading is impossible. According to International Critical Tables (*8*), hexanitrodiphenylamine decomposes at 250° C. Colver (*4*) states that the compound's melting point is identical with the decomposition point which lies between 240° and 250° C.

If the yield when nitrating diphenylamine were 100 per cent, the factor would be much lower, but the established factor of 0.4259 represents a yield of about 90 per cent. If all conditions of the test are kept constant there will be practically no change in this yield.

Conversion Products of Diphenylamine in Powders

In the slow decomposition of powder containing diphenylamine as a stabilizer, there are several steps in the breaking down of the diphenylamine which are considered to exist at different ages of the powder. Beginning with the pure diphenylamine, the first step is the formation of diphenylnitrosamine, next nitrodiphenylnitrosamine, next dinitrodiphenylamine, and the final product is trinitrodiphenylamine (*5*). The most generally accepted stages of conversion may be shown by the following formulas (*9*):

(1) $(C_6H_5)_2N-H$ — Diphenylamine; Molecular weight, 169.1; Melting point, 52.5° C.

(2) $(C_6H_5)_2N-N=O$ — Diphenylnitrosamine; Molecular weight, 198.10; Melting point, 66.0° C.

(3) $(C_6H_4NO_2)(C_6H_5)N-N=O$ — Nitrodiphenylnitrosamine; Molecular weight, 243.0; Melting point, 130.0° C.

(4) $(C_6H_4NO_2)_2N-H$ (2,4′) (4,4′) — Dinitrodiphenylamine; Molecular weight, 259.0; Melting point, 156.5° C.

(5) $(C_6H_3(NO_2)_2)(C_6H_4NO_2)N-H$ (2,4,4′) (2,4,2′) — Trinitrodiphenylamine; Molecular weight, 304.0; Melting point, 181° C.

Table IV proves that if, in the natural aging of the powder, there were present any one of these nitrodiphenylamines, the results by the nitration method would include both the diphenylamine as such and the combined diphenylamines.

In most powders the nitration method gives accurately the amount of diphenylamine, but in old or reworked powders it gives only the total diphenylamine added and fails to show the amount of available or active diphenylamine left. The active diphenylamine includes both diphenylamine and diphenylnitrosamine. Therefore, other methods were developed for determining active diphenylamine and are described below.

Soda Distillation for Active Diphenylamine

The development of the soda distillation method for determining active diphenylamine in smokeless powder is based upon Dreger's method (*6*) of dissolving the powder in sodium hydroxide solution and distilling with steam with subsequent bromination of the ether extract. Various modifications of this method were tried: (1) varying percentage of sodium hydroxide solution from 5 to 40, (2) varying amount of solution used, (3) varying time of distillation, (4) varying speed of distillation, (5) varying amount of bromine used, (6) using ether instead of alcohol, (7) using acetic acid as bromination medium, and (8) varying size of flasks, length of condenser, etc.

Inasmuch as only diphenylamine and diphenylnitrosamine are valuable as stabilizers, it was necessary to verify the bromination method to see if these two compounds could be separated from the powder together and determined ac-

Table V. Bromination Results on Diphenylamine in Ether Solution

Weight of Diphenylamine	Theoretical Bromine Necessary to Brominate	Bromine Added			Diphenylamine (basis 5 g. powder)	
				% Excess by weight	Added	Found
Gram	*Gram*	*Gram*	*Cc.*		%	%
0.015	0.057	0.64	0.20	1000.0	0.30	0.30
0.025	0.10	0.64	0.20	540.0	0.50	0.31 0.51 0.50
0.050	0.19	0.64	0.20	237.0	1.00	0.49 1.01
0.075	0.29	0.64	0.20	120.0	1.50	1.02 1.51 1.52
0.100	0.38	0.64	0.20	70.0	2.00	1.98
0.050[a]	0.19	0.64	0.20	237.0	1.00	1.00
0.050[a]	0.19	0.64	0.20	237.0	1.00	1.00

[a] 0.1 gram of nitrocellulose was added to these samples and then after evaporation 10 grams of sodium hydroxide in 100 cc. of water were added to dissolve the nitrocellulose.

Table VI. Results on Powders

Sample	Total Volatiles	Diphenylamine Added to Powder	Diphenylamine Found
	%	%	%
6	3.45	1.00	0.96, 0.95
16	2.65	1.00	0.97, 0.97
8	4.55	1.00	1.04, 1.04
13	4.55	1.00	0.98, 1.00

Table VII. Bromination of Diphenylamine and Its Nitro Compounds by Bromine in Ether Extract

(After distilling with steam and 10 per cent sodium hydroxide)

Compounds Used	Compound Taken	Diphenylamine Equivalent	Bromo Compound Found	Diphenylamine Yield[a]	Diphenylamine Found[b]
	Gram	*Gram*	*Gram*	%	%
Diphenylamine	0.0500	0.05	0.1435	100	1.00
Diphenylnitrosamine	0.0585	0.05	0.1444	100	1.00
Nitrodiphenylnitrosamine	0.0719	0.05	0.0035	2.4	0.02
Dinitrodiphenylamine	0.0766	0.05	0.0020	1.4	0.01
Trinitrodiphenylamine	0.0930	0.05	0.0000	0	0

[a] Factor 0.3487 used for conversion.
[b] On basis of 5 grams powder.

Table VIII. Bromination of Nitro Compounds of Diphenylamine with Bromine in Ether and Glacial Acetic Acid

Compounds Used for Bromination	Weight Taken	Weight Found	Color of Compound Found	Molecular Weight of Compound Taken	Melting Point of Compound Taken	Melting Point of Compound Found
	Gram	*Gram*			° *C.*	° *C.*
		Bromination in Ether				
Nitrodiphenylnitrosamine	0.0719 0.0719 0.0719	0.0910 0.0930 0.0937	Dark brown	243	131	112
Dinitrodiphenylamine	0.0766 0.0766	0.1000 0.1044	Orange	259	157	138
Trinitrodiphenylamine	0.0930 0.0930	0.0920 0.0890	Golden, same as original	304	188	187
		Bromination in Glacial Acetic Acid				
Nitrodiphenylnitrosamine	0.0719	0.1354	Bright yellow	243	131	205
Dinitrodiphenylamine	0.0766	0.1113	Orange and dark brown mixed	259	157	142
Trinitrodiphenylamine	0.0930	0.0970	Yellow or golden	304	188	185

curately. As in the nitric acid method, standards were run by taking known weights of pure diphenylamine (0.05 gram in each case) and running them through after adding 5 grams of dry nitrocellulose.

Results when following the Dreger method were not satisfactory, so ether was used instead of an alcohol medium in which to brominate. Too large a sample is required in the Dreger method as well as too long a time for distillation. Table V shows clearly that excellent results were obtained with ether, and that 0.2 cc. of bromine is ample for powders containing as high as 2 per cent of diphenylamine.

After determining the safe amount of bromine necessary and the best solvent, actual tests were made on samples of powder containing 1 per cent of diphenylamine.

Procedure. (1) Distillation of powder with steam in sodium hydroxide solution, (2) extraction of distillate with ether, (3) bromination of diphenylamine and evaporation with air, and (4) boiling with 5 per cent sodium hydroxide to break up lumpy tetrabromodiphenylamine.

Exactly 5 grams of sliced powder (total volatiles known) are weighed, transferred to a 500-cc. Ladenburg flask and 200 cc. of 10 per cent sodium hydroxide solution are added. The flask is supported on an electric heater set at 1 ampere (Central Scientific Co. No. 533 asbestos top with 6.25 cm., 2.5 inch, diameter opening). The side arm of Ladenburg flask is connected to a 50-cm. (20-inch) water condenser, at other end of which is an adapter leading into a 1000-cc. separatory funnel to catch the distillate. Steam is passed into the Ladenburg flask by means of a glass tube, one end of which reaches to the bottom of the soda solution in the flask, the other end going through a Kjeldahl connecting bulb into a 1-liter flask containing water and set on an electric flask heater (Fisher Scientific Co., Type H, 550 watts). Steam distillation is continued until 500 cc. collect in the receiver, then the apparatus is disconnected and allowed to cool. The condenser and adapter tube are washed out with about 85 cc. of ether into the separatory funnel, 10 grams of sodium chloride are added, the funnel is shaken well, and allowed to stand until water layer is clear. The water layer is drawn off and the ether layer caught in a dry 250-cc. beaker. The extraction is repeated with another 85 cc. of ether. To the combined ether extracts 0.2 cc. of pure bromine is added carefully, all ether and bromine are evaporated off on low-temperature bath at about 75° C. with air, 100 cc. of 5 per cent sodium hydroxide are added, boiled 2 minutes, filtered on a weighed Gooch crucible, and washed well with hot water. The crucible is dried in oven 1 hour at 105° C., cooled, and weighed. The precipitate is tetrabromodiphenylamine.

$$\text{Per cent of active diphenylamine} = \frac{\text{weight of ppt.} \times 0.3487 \times 100}{\text{weight of powder less total volatiles}}$$

The powders in Table VI are all new and show no loss of diphenylamine.

Diphenylamine and diphenylnitrosamine distill over with steam 100 per cent. Each test in Table VII represents the bromination of 0.05 gram of diphenylamine or its equivalent weight of nitro compound. For example, 0.093 gram of trinitrodiphenylamine represents the weight of this substance which would be formed in 5 grams of a 1 per cent diphenylamine powder, providing the powder has aged to such an extent that all of the diphenylamine had changed over to this form.

According to previous investigators (*5*), no nitro compounds of diphenylamine beyond the stage of the trinitrodiphenylamine have ever been found in old powders, so in this investigation it was not necessary to try the effect of the tetranitro or higher nitrated diphenylamines when treated with bromine.

In the case of the distillation and bromination of nitrodiphenylnitrosamine and dinitrodiphenylamine, a small weight of residue (0.0035 and 0.0020 gram, respectively) was found. Calculating this to a basis of diphenylamine in 5 grams of sample gives results of 0.02 and 0.01 per cent of diphenylamine. It is unlikely that at any time during the natural aging of a powder all the diphenylamine would be converted to either nitrodiphenylnitrosamine or dinitrodiphenylamine. and therefore this small percentage would not vitiate the results sufficiently to justify discarding the method or making a correction for that amount.

To determine the effect of brominating the three nitrodiphenylamines in ether and acetic acid, known weights of these compounds were dissolved in these solvents and 0.2 cc.

of bromine was added. Three other tests were made by the regular volumetric bromination method, using alcohol as a medium, with potassium bromate-bromide solution. The first two compounds are brominated to some extent but the trinitrodiphenylamine is not.

In the volumetric tests no definite end point could be obtained in the case of nitrodiphenylnitrosamine and only a small titration of 2.6 cc. of sodium thiosulfate, equivalent to 0.005 gram of diphenylamine, was found in the case of dinitrodiphenylamine. These results throw out the direct bromination of powder after extraction when the powders contain any nitrodiphenylnitrosamine or dinitrodiphenylamine. On new powders direct bromination of the ether extraction will give accurate amounts of diphenylamine in the powder.

Table VIII clearly establishes the fact that the direct bromination of the ether extract of any powder which contains nitrated diphenylamines beyond the diphenylnitrosamine stage is not an accurate method for determining the total diphenylamine or the unchanged or active diphenylamine.

Extraction Method

Old powders which were thought to contain some nitrodiphenylamines were run by the distillation method. The residue in the flask which also contained some sodium hydroxide, water, and the saponification products of the powder, was taken to dryness in a beaker, neutralized with nitric acid, and carried from hereon by the regular nitric acid method. The large amount of salts present interfered with this test. Extraction of the nitro compounds with ether also proved unsuccessful. Softening of the powder with ether was tried with subsequent extraction in Soxhlet extraction apparatus, and found to be successful.

Procedure. (1) Soften powder with ether and little alcohol, (2) extract with ether in Soxhlet with thimble, (3) distill extract with steam, (4) extract distillate with ether and brominate, and (5) evaporate residue in distilling flask and nitrate residue in glacial acetic acid.

Five grams of powder, total volatiles known, are weighed into a conical 100-cc. weighing bottle. Powder may be in whole grains if small size or in slices as needed for a fair sample. Fifty cubic centimeters of ether, prepared by washing with water and distilling are added and sample is placed in ice box for 24 hours; then 0.5 to 1 cc. of alcohol is added and let stand 24 hours more. This treatment will soften and swell the powder so that extraction is easy without having the powder break up. Some samples may require slightly more alcohol, but it is better to give more time soaking.

When soft, the sample is transferred to a 30 × 80 mm. paper thimble in Soxhlet extractor using a long-tube aluminum funnel with tube wide enough to allow powder to fall through freely; the powder is washed into the thimble with ether until the extractor flask, holding 250 cc., is half full.

The powder is extracted 6 hours on a water bath and extract transferred to a 200-cc. long-neck side-outlet distilling flask, using 25 cc. of water, and distilled with steam using the same condensing and heating arrangements as in previous method. The ether is first carefully distilled at low heat and finally the water in the distilling flask is heated and steam passed through until ether and water collected are about 400 cc.

The distillate is extracted and brominated exactly as in the previously described method. The residue in the distilling flask contains all nitro compounds above the diphenylnitrosamine. The contents of the distilling flask are transferred to a 250-cc. beaker and evaporated to dryness. The dried flask is washed out with glacial acetic acid to dissolve nitro compounds, heating on steam bath as necessary.

Just 10 cc. of total acetic must be used for this. The washings are poured into the beaker containing the dried residue from the distilling flask; the flask is then washed out with two 10-cc. portions of nitric acid (sp. gr. 1.42) and these washings are added to the acetic acid washings with 3 grams of air-dry nitrocellulose. The nitro compounds are determined from this point by the regular nitric acid method. The product is hexanitrodiphenylamine, for which the factor to convert to equivalent diphenylamine is 0.4259. When powders are new this method may be so far modified as to omit parts 3, 4, and 5 of procedure and brominate directly in the ether which has been used to extract the powder in part 2.

Table IX. Results of Bromination of Diphenylamine by Volumetric Method

	Diphenylamine[b] Added	Diphenylamine[b] Found
	%	%
Known standard[a]	1.00	1.00
	1.00	0.99
	1.00	0.99
Sample 14	0.99	0.99
	0.99	0.99
	0.99	0.99
Sample 66	0.99	0.96
	0.99	0.96
Sample 6	0.99	0.98
	0.99	0.98
	0.99	0.98
Sample 1614	0.99	0.98
	0.99	0.98
	0.99	0.98

[a] 0.05 gram of diphenylamine, 0.50 gram of plasticizer *a*, 0.25 cc. of plasticizer *b*, 0.10 grams of nitrocellulose, and 25 cc. of ether.
[b] Basis of 5 grams of powder.

Table X. Bromination of Three Nitrodiphenylamines in Alcohol by Means of Potassium Bromate-Bromide Solution

	Weight Taken	Sodium Thiosulfate Used	Diphenylamine
	Gram	*Cc.*	*Gram*
Nitrodiphenylnitrosamine	0.0719	..	No definite end point
Dinitrodiphenylamine	0.0766	2.6	0.005
Trinitrodiphenylamine	0.0930	Nil	Nil

Table XI. Tests on Powders by Volumetric Method

Method	Diphenylamine
	%
Sample 8, newly made powder	
Volumetric	0.98, 1.00
Nitric acid	0.99
Soda distillation	0.99
Special powder No. 1 with plasticizers, a new powder	
Volumetric	0.97
Soda distillation	0.98
Extraction	0.98

Specially Prepared Powders Containing Certain Plasticizers

The nitration method has been found inapplicable to powders containing certain plasticizers, but the soda distillation, extraction, and volumetric methods give good results when slightly modified as follows:

Soda Distillation Method for Special Powders. The distillation is carried out with 20 per cent sodium hydroxide-water solution with extraction and bromination as heretofore described to the point where ether is evaporated from the bromo compound; when the bromo compound is dry, 40 cc. of 95 per cent ethyl alcohol are added and the mixture is brought to the boiling point. Forty cubic centimeters of water are then added and the beaker is left on the steam bath for 10 minutes. The bromo compound is filtered warm on a Gooch crucible and washed with 80 cc. of warm 47.5 per cent ethyl alcohol (by volume) and finally with hot water. Drying and weighing of the tetra-bromo compound are as for nitrocellulose powder. Diphenylamine in these powders is reported on the basis of powder with moisture and volatile solvent.

$$\text{Per cent of diphenylamine} = \frac{\text{weight of bromo compound} \times 0.3487 \times 100}{\text{weight of powder}}$$

Extraction Method for Special Powders. The powder is softened and extracted with ether as for straight nitrocellulose powder; the extract is transferred to a 250-cc. beaker, bromi-

TABLE XII. COMPARISON OF RESULTS

Method	Diphenylamine Found (corrected for volatiles)
	%
A. Soda distillation	0.38 active
B. Extraction with ether, then separation with steam and bromination	0.36 active
C. Extraction with ether, then direct bromination	0.64
D. Same as *C* except using volumetric method	0.30
E. Residue in flask from *B* by nitric acid method	0.46 inactive
F. Total diphenylamine by nitric acid method	0.85
Total diphenylamine by *F* less amount by *A* = converted diphenylamine	0.47 inactive

TABLE XIII. COMPARISON OF RESULTS ON REWORKED POWDERS

(Results on four 5-gram samples of reworked powders using the nitric acid, distillation, and extraction methods)

Method	Diphenylamine Found (corrected) 1	2	3	4
	%	%	%	%
Nitric acid	0.54	0.54	0.54	0.52
Soda distillation	0.49	0.46	0.45	0.45
	0.50	0.46	0.46	0.45
	0.51	..	0.47	..
Av.	0.50	0.46	0.46	0.45
Extraction with ether, then separation with steam and bromination	0.49	0.45	0.48	0.45
	0.50	0.45	0.45	0.45
Av.	0.50	0.45	0.47	0.45
Residue in flask from extraction by nitric acid method	0.05	0.10	0.04	0.05
Sum of active and inactive diphenylamine	0.55	0.55	0.51	0.50

TABLE XIV. COMPARISON OF RESULTS ON NEW POWDERS

Powder Sample	Diphenylamine Found: Soda distillation, Analyst 1	Soda distillation, Analyst 2	Extraction method, Analyst 1	Extraction method, Analyst 2
	%	%	%	%
18	1.04	1.04	1.06	1.03
1	0.98	0.98	0.98	0.98
51	0.94	0.95	0.97	..
6	..	0.96	0.97	0.98

nated, and the bromo compound dried as for straight nitrocellulose powder. Forty cubic centimeters of 95 per cent ethyl alcohol are then added, the liquid is brought to the boiling point, 40 cc. of water are added, and the beaker is left on the steam bath for 10 minutes. The liquid is filtered on a Gooch crucible and washed with 80 cc. of warm 47.5 per cent ethyl alcohol (by volume), dried 1 hour at 105° C., cooled, and weighed. The crucible is washed with hot benzene, dried, and reweighed; the difference in weight is bromo compound.

$$\text{Per cent of diphenylamine} = \frac{\text{weight of bromo compound} \times 0.3487 \times 100}{\text{weight of powder}}$$

The warm alcohol solution dissolves all plasticizer compounds but not the tetrabromodiphenylamine. The hot benzene dissolves the tetrabromodiphenylamine but none of the nitrocellulose which comes through during the extraction of the powder in Soxhlet apparatus.

VOLUMETRIC METHOD FOR SPECIAL POWDERS. This method is identical with the volumetric method for straight nitrocellulose powders, described below.

Table IX gives results of tests of bromination of diphenylamine by the volumetric method in ethyl alcohol in the presence of certain plasticizers and nitrocellulose and in specially prepared powders containing these plasticizers. The presence of plasticizers does not interfere in any way with the bromination of the diphenylamine.

Volumetric Method for Smokeless Powders

This method (*3*) was verified for accuracy by using known amounts of materials.

In two separate flasks 0.05 gram of diphenylamine and 0.0585 gram of diphenylnitrosamine are dissolved in ether, 5 grams of nitrocellulose are added, the ether is evaporated with air, and 50 cc. of ethyl alcohol are added to each. Twenty cubic centimeters of standard 0.2 *N* potassium bromate-bromide solution are added, the flasks cooled in ice water, 10 cc. of concentrated hydrochloric acid added, and the flask is placed in ice water for 2 minutes. Ten cubic centimeters of 10 per cent potassium iodide are added and after 3 minutes the mixture is titrated with 0.1 *N* sodium thiosulfate, using starch as indicator.

A = cc. used for blank = 38.7
B = cc. used in titration = 14.2

C = cc. necessary 24.5
N = normality of sodium thiosulfate = 0.0985
W = weight of sample taken = 5 grams
1 cc. of N sodium thiosulfate = 0.021136 gram of diphenylamine

$$\text{Per cent of diphenylamine in powder} = \frac{(A - B)N \times 0.021136 \times 100}{W}$$

$$= \frac{(38.7 - 14.2)0.0985 \times 0.021136 \times 100}{5} = 1.01$$

With the diphenylnitrosamine it was difficult to get an end point. A fair end point was finally reached, but when calculated it amounted to a small titration of only 4.3 cc., whereas the titration should have been 23.85 cc. as with the former test. Calculating this titration gives a weight of 0.009 gram of diphenylamine found or 0.18 per cent in the powder, which is a yield of only 18 per cent of diphenylamine.

If diphenylnitrosamine is present in the extracted powder, only a small proportion of it will be titrated. In the first place, a good end point is difficult to arrive at, perhaps on account of a liberation of nitrous oxides during the reaction. If an unknown sample of powder happened to contain this nitrosamine, the volumetric bromination method would be inaccurate but, on new or fairly new powders, this method is acceptable for straight nitrocellulose powders and specially prepared powders containing plasticizers. (Table X.)

As far as the investigation has gone, the volumetric method gives good results even in old powders, providing they do not contain any diphenylnitrosamines. (Table XI.)

Comparison of Results by Four Methods

Sample 6 was heated for 350 days at a temperature of 65.5° C. This heating caused the powder to age very fast and Table XII shows results determined by all the methods described in this paper. Total volatiles equaled 0.98 per cent.

In the case of *D*, the end point was difficult to determine, and thus the result is not reliable. Test *C* gave 0.64 per cent diphenylamine. This confirms previous tests that total diphenylamine in an old powder cannot be found by extraction of the powder with subsequent bromination. The other tests check very well. The sum of *A*, active diphenylamine, and *E*, inactive diphenylamine—0.38% + 0.46% = 0.84%—checks *F*, 0.85 per cent total of active and inactive diphenylamine in the powder.

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A Modified Persulfate-Arsenite Method for Manganese

With Special Reference to Steel Analysis

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A method for the determination of manganese in steel is proposed in which the permanganic acid formed by the oxidation of the sample with ammonium persulfate, in the presence of phosphoric acid with silver as catalyst, is titrated with a reducing solution containing equivalent amounts of sodium arsenite and sodium nitrite instead of with the customary sodium arsenite alone. With the mixed reducing solution, heptavalent manganese is reduced to the divalent condition, and the solution therefore becomes colorless at the end point instead of yellow or brown as when arsenite alone is used for the titration. Small amounts of chromium, vanadium, nickel, and molybdenum do not interfere. Silver must be precipitated as the chloride before the titration can be made.

THE persulfate-arsenite method, in which the permanganic acid formed by the oxidation of manganous ion in acid solution with ammonium persulfate is titrated with sodium arsenite using silver salt as catalyst, has long been a favorite routine method for the determination of manganese in iron and steel. Bright and Larrabee (*1*) have improved the method to the extent that the results obtained by it compare very favorably with those obtained by the standard bismuthate method. These authors oxidize manganese with persulfate in the presence of phosphoric acid, which permits the complete oxidation of much more manganese than was formerly possible, and titrate the permanganic acid with sodium arsenite. Permanganic acid is reduced by arsenite to a more or less indefinite valence state corresponding approximately to $Mn^{+3.3}$. Manganese in this state of oxidation has a yellowish or brownish color and it is therefore sometimes difficult to detect the exact end point when relatively large amounts of manganese are present (the end point may be found potentiometrically in such cases) (*2*, *6*), especially if the operator has not had experience with the titration.

It would be desirable to titrate the permanganic acid formed in the persulfate oxidation with a reagent that would reduce manganese to the manganous condition—i. e., to a colorless form. Such a reagent must not react appreciably with the persulfate left after the oxidation, nor with chromate, vanadate, and other substances possibly present in an oxidized solution of a steel sample. Alkali nitrites when added to an acid permanganate solution reduce heptavalent manganese to the divalent state without giving a visible trace of the yellow or brown intermediate oxides. However, the reaction is slow, and it is necessary to warm the solution to about 40° C. to obtain fairly satisfactory results. Without modification the reaction is not suitable for the determination of manganese in ferrous products. It was found in the present work that a suitable reagent for the reduction of permanganic acid to colorless manganous salt could be obtained by mixing sodium arsenite and sodium nitrite in equivalent amounts. The arsenite and nitrite exert a peculiar reciprocal influence upon each other: On the one hand, the nitrite prevents the formation of the intermediate oxides of manganese in the reduction of permanganic acid by the arsenite, and the arsenite, on the other hand, greatly increases the speed of interaction of nitrite and permanganic acid, so that the titration with the mixed reagent can be made at room temperature.

Experimental

TITRATION OF POTASSIUM PERMANGANATE WITH SODIUM ARSENITE–SODIUM NITRITE. Known amounts of potassium permanganate solution standardized against Bureau of Standards sodium oxalate were titrated under various conditions with the mixed titrating reagent sodium arsenite–sodium nitrite. In all the experiments except those of (1) below, a standardized reducing solution was used in which the ratio of arsenite to nitrite was 1 to 1 (based on reducing normality).

Equal volumes (accurately measured) of sodium arsenite and sodium nitrite solutions, both approximately 0.05 *N*, were mixed to give a reducing solution which was thus 0.05 *N*. The exact normality of the mixed reducing solution was calculated from the normalities of the component solutions. The arsenite solution was prepared by dissolving pure arsenious oxide in a slight excess of sodium hydroxide and neutralizing the resulting solution with sulfuric acid; it was standardized by titration with standard permanganate in acid solution, using a trace of potassium iodate as catalyst according to the method of Lange (*5*). The sodium nitrite solution (prepared by dissolving C. P. sodium nitrite in water) was standardized by a modification of the method of Höeg and Klemenc (*3*, *4*) as follows: A measured volume of the nitrite solution was allowed to flow into a partially evacuated flask containing a measured excess of standard potassium permanganate solution acidified with sulfuric acid. The excess of permanganate was determined iodometrically after the mixture had stood for 5 minutes at room temperature, followed by warming to 40° C.

The influence of the following factors on the titration of permanganate by the mixed reagent was investigated.

1. The composition of the standard solution (the ratio of sodium arsenite to sodium nitrite).

Without giving the numerical results of this set of experiments, it may be stated that the standard reducing solution in which the arsenite-nitrite ratio was 1 to 1, prepared as just described, gave the most satisfactory results. When the ratio of arsenite to nitrite in the reducing solution was 1 to 2, the reaction with permanganate was so slow that the end point could not be satisfactorily determined at room temperature, whereas when the ratio was 2 to 1 the appearance of a brownish tinge in the solution titrated indicated the formation of small amounts of the intermediate oxides of manganese.

2. The influence of nitric and phosphoric acids, iron, etc.

To test the effect of substances that would be present after the oxidation of a steel sample by the method of Bright and Larrabee (*1*), 30 ml. of sulfuric-phosphoric-nitric acid mixture (see Recommended Procedure) were boiled for 1 minute to remove any oxides of nitrogen present, cooled to 20° to 25° C., and diluted with water plus the indicated volume of standard permanganate together with the indicated added substance to a volume of 100

ml. Before the titration was made, 10 ml. of 12 *N* sulfuric acid were added to bring the acidity of the solution well above 3 *N*. Table I contains the results of this series of experiments.

TABLE I. VALUE OF ARSENITE-NITRITE/PERMANGANATE RATIO IN PRESENCE OF SULFURIC-NITRIC-PHOSPHORIC ACID MIXTURE AND ADDED SUBSTANCES

(Theoretical value of arsenite-nitrite/permanganate ratio = 1.164)

No.	Volume of ca. 0.05 *N* $KMnO_4$ Titrated *Ml.*	Addition	Ratio Arsenite-Nitrite/Permanganate
1	5		1.164
			1.156
			1.164
2	10		1.160
			1.153
3	10	1 g. $(NH_4)_2S_2O_8$	1.163
4	10	1 g. $(NH_4)_2S_2O_8$ + 1 ml. 0.5 *M* $AgNO_3$	No end point; brown color
5	10	1 ml. 0.5 *M* $AgNO_3$ + 2 ml. 0.5 *M* NaCl	1.160
6	10	1 g. $(NH_4)_2S_2O_8$, 1 ml. 0.5 *M* $AgNO_3$ + 2ml. 0.5 *M* NaCl	1.163
7	10	As in (5) + 1 g. Fe as ferric alum	1.154
8	10	As in (5) + 5 ml. 0.1 *N* K_2Cr_2O + 5 ml. 0.05 *N* NH_4VO_3	1.160
9	20		1.155
10	25		1.151

TITRATION OF REDUCED POTASSIUM PERMANGANATE SOLUTIONS OXIDIZED WITH AMMONIUM PERSULFATE. Measured amounts of standard potassium permanganate solution were added to 30 ml. of the sulfuric-phosphoric-nitric acid mixture, sometimes together with 1 gram of iron as electrolytic iron or as ferrous ammonium sulfate. When no iron was added, the permanganate was reduced by adding a slight excess of sodium bisulfite. The reduced manganese solution was treated with silver nitrate and ammonium persulfate, and oxidized exactly as described below; the titration was also made as there described. These data are of importance in connection with the standardization of sodium arsenite–sodium nitrite solutions, especially as regards the dependence of the titer upon the concentration of permanganate present. The results are given in Table II.

DETERMINATION OF MANGANESE IN STEELS BY PROPOSED PROCEDURE. The sodium arsenite–sodium nitrite solution was prepared and standardized as described in the Recommended Procedure. Bureau of Standards steels were used to test the performance of the method, and the results are reported in Table III.

Discussion of Experimental Results

The following important conclusions may be drawn from the experimental work:

The ratio of sodium arsenite to sodium nitrite in the standard reducing solution should be approximately 1 to 1 (normality ratio); the ratio may be varied between 0.8 to 1 and 1.2 to 1 without ill effect.

The titration of permanganic acid with the mixed reducing solution must not be made too rapidly. The reaction between nitrite and permanganate in the presence of arsenite is not instantaneous. If the standard reducing solution is added too rapidly, free nitrous acid is formed and may be partially lost by volatilization, and in any event irregular results are then likely to be obtained, owing to the fact that the true end point may be overstepped.

It is especially important to add the standard solution slowly near the end point.

With a sufficiently high acidity (greater than 3 *N*) and proper speed of titration, it is found that the reaction between the mixed reagent and permanganate is nearly stoichiometric according to the equations:

$$2MnO_4^- + 5As^{+++} + 16H^+ \longrightarrow 2Mn^{++} + 5As^{+++++} + 8H_2O$$

$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{++} + 5NO_3^- + 3H_2O$$

Silver when present with persulfate must be precipitated as the chloride by the addition of a slight excess of sodium chloride or hydrochloric acid before permanganate can be titrated with the mixed reagent. Otherwise permanganate is not reduced to manganous salt and a brown solution is obtained.

When small amounts of permanganate are titrated, slightly more arsenite-nitrite is required than is demanded by the preceding equations, especially at low acidities, whereas the theoretical value is rather closely approached when the permanganate concentration is larger than about 0.005 *N*. Although it has been found that the ratio of arsenite-nitrite to permanganate depends upon the amount of permanganate titrated, the ratio is sufficiently constant to permit the use of the mixed reducing solution in the determination of manganese in steel (Table II).

In determining manganese in a ferrous material by titrating the permanganic acid formed in the oxidation of the solution with ammonium persulfate, the arsenite-nitrite solution should be standardized under the same conditions that obtain in the titration of the oxidized steel sample—i. e., a measured amount of standard potassium permanganate solution should be reduced and then reoxidized with ammonium persulfate in the presence of iron. A slight difference is found in the titer of the arsenite-nitrite solution if iron is omitted in the standardization (columns 1 and 2, Table II). Iron should be added as the pure metal containing minimal amounts of manganese (electrolytic iron), and not as ferrous ammonium sulfate or ferric alum, because the ammonium salt introduced in the latter case affects the results slightly

TABLE II. EFFECT OF IRON IN STANDARDIZATION OF SODIUM ARSENITE–SODIUM NITRITE AGAINST STANDARD POTASSIUM PERMANGANATE

(Corrections have been applied for manganese in the added iron.)

Manganese Taken	Manganese Value of 1 Ml. of Sodium Arsenite–Sodium Nitrite Solution: No Fe added	1 g. Fe as electrolytic iron added	1 g. Fe as $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ added
Mg.	*Mg.*	*Mg.*	*Mg.*
1.20	0.49	...	0.51
3.01	0.510	0.507	0.514
	...	0.503	0.518
6.02	0.515	0.511	0.517
	0.514	0.512	0.516
9.03	0.513	0.513	0.516
	0.514	0.513	0.517
12.04	0.519	0.516	0.518
	0.517	0.517	0.517
15.05	0.519	0.519	0.523
	0.519	0.518	0.520

TABLE III. DETERMINATION OF MANGANESE IN BUREAU OF STANDARDS STEELS BY PROPOSED METHOD[a]

Standard Steel No.	Certificate Value	Mn Found	Difference	Type of Steel
	%	%	%	
15a	0.372	0.374	+0.002	B. O. H., 1 per cent carbon
		0.373	+0.001	
14b	0.493	0.498	+0.005	B. O. H., 0.8 per cent carbon
9c	0.668	0.665	−0.003	Bessemer, 0.2 per cent carbon
9c	1.23[b]	1.24	+0.01	Bessemer, 0.2 per cent carbon
	1.26[b]	1.27	+0.01	with additional manganese
	1.50[b]	1.49	−0.01	added as permanganate
32a	0.244	0.242	−0.002	Chrome-nickel (0.89 per cent Cr; 1.57 per cent Ni)
111	0.662	0.659	−0.003	Nickel-molybdenum (1.75 per
		0.665	+0.003	cent Ni; 0.215 per cent Mo)
30a	0.805	0.82	+0.015	Chrome-vanadium (1.03 per
		0.81	+0.005	cent Cr; 0.20 per cent V)

[a] Except for No. 9c with added amounts of manganese, the titer of the arsenite-nitrite solution was obtained by titrating 10 ml. of approximately 0.05 *N* permanganate. The titer used in calculating the results of the titrations of 9c with 1.23, 1.26, and 1.50 per cent of manganese was obtained by standardization against 25 ml. of 0.05 *N* permanganate. All standardizations were made in the presence of 1 gram of electrolytic iron.

[b] Calculated from the known amount of potassium permanganate solution added.

(columns 2 and 3, Table III). When the most accurate results are not required, the standardization may be made in the absence of iron. Since the titer of the reducing solution depends upon the amount of permanganate titrated, the amount of the latter taken in the standardization should correspond approximately to the quantity of manganese present in the sample when the best results are desired, especially when the percentage of manganese in the sample is larger than 0.8 or 0.9 per cent. In most cases it will be satisfactory to take 10 ml. of 0.05 *N* potassium permanganate solution (corresponding to 0.55 per cent manganese in a 1-gram iron or steel sample) for the standardization. The titer of the reducing solution thus obtained can be applied in the calculations when 1-gram samples containing from 0.3 to 0.8 per cent of manganese are taken, without introducing an error exceeding ±0.005 per cent of manganese from the lack of proportionality (column 2, Table II).

The maximum amount of manganese that may be present in the solution titrated is 15 mg. per 100 ml. when iron is present. Above this concentration the reduction of permanganic acid to manganous salt no longer proceeds smoothly, but becomes very slow. In the absence of iron more manganese may be present.

Alloying elements such as chromium, vanadium, nickel, and molybdenum do not interfere when present in the usual amounts, except that the end point is less sharp when the solution is colored.

The reproducibility of the method is moderately good, as Tables II and III indicate, and the accuracy is satisfactory for most purposes.

The arsenite-nitrite solution is fairly stable. A 0.05 *N* solution having a pH of 6.8 decreased in strength by 1.5 per cent after standing in the dark for one year.

The method of Bright and Larrabee for the oxidation of manganese with ammonium persulfate has been found to be highly satisfactory and has been incorporated in the procedure given below.

Recommended Procedure for Manganese in Steels

Reagents. (1) Acid mixture (recommended by Bright and Larrabee): Water, 525 ml.; sulfuric acid, concentrated (sp. gr. = 1.84), 100 ml.; phosphoric acid, 85 per cent, 125 ml.; and nitric acid, concentration (sp. gr. = 1.42), 250 ml. First add the sulfuric acid to the water, cool, and then add the nitric and phosphoric acids. (2) Silver nitrate solution, 0.1 *M*. (3) Ammonium persulfate solution, 25 grams (of 95 per cent salt) in 80 ml. of water. Ammonium persulfate slowly decomposes in solution and therefore this solution should not be kept for more than 2 or 3 days. (4) Sodium chloride solution, 0.2 *M*. (5) Sulfuric acid, 12 *N*.

Standard Solutions. (1) Sodium arsenite–sodium nitrite, 0.05 *N*. Dissolve 2.5 grams of pure arsenic trioxide in 25 ml. of 4 *N* sodium hydroxide solution, dilute to 200 ml., add slightly more than enough dilute sulfuric acid to neutralize the hydroxide, and then a slight excess of sodium bicarbonate to neutralize the acid (the solution should finally be neutral to litmus paper). Dissolve 0.85 gram of sodium nitrite in the solution thus obtained and dilute to 1 liter. (2) Potassium permanganate, 0.05 *N*. Prepare and standardize against pure dry sodium oxalate in the usual manner.

Standardization of Sodium Arsenite–Sodium Nitrite Solution. Pipet 10 ml. of standardized 0.05 *N* potassium permanganate solution (for the best results the amount of permanganate taken should correspond approximately to the amount of manganese in the material under test) into a 250-ml. Erlenmeyer flask, and add 1.0 gram of electrolytic iron of known manganese content and 30 ml. of the sulfuric-phosphoric-nitric acid mixture. Warm to hasten solution, and finally boil for 2 to 3 minutes to expel oxides of nitrogen. Then add 50 ml. of cold water, 5 ml. of silver nitrate solution, and 10 ml. of ammonium persulfate solution. Heat to boiling, and boil for 30 to 45 seconds. Immediately cool the flask and its contents to 20° to 25° C. by placing in water. Add 5 ml. of sodium chloride solution and 10 ml. of 12 *N* sulfuric acid. Then titrate with arsenite-nitrite solution. Run in the reducing solution at a uniform rate not exceeding 5 or 6 ml. per minute, swirling the liquid in the flask continuously until the solution has become pale pink, and then continue the addition more slowly, allowing about 5 seconds between drops. When very near the end point as indicated by the very pale pink color, allow approximately 10 seconds between drops or fractions of a drop. This slow addition is required only for the last few drops. The end point is reached when the color changes abruptly to white (suspended silver chloride). If the titration has been correctly performed, a drop of 0.05 *N* permanganate solution added after the end point has been reached will give a coloration persisting for at least 3 minutes.

Determination. Dissolve a 0.9- to 1.1-gram sample of steel in 30 ml. of the acid mixture and then proceed as directed in the standardization (beginning with the second sentence).

Notes

If an accuracy greater than ±0.01 per cent of manganese is not required, the addition of iron in the standardization may be omitted. Then standardize as follows:

Transfer 30 ml. of acid mixture to a 250-ml. Erlenmeyer flask and add 50 ml. of water, 5 ml. of silver nitrate solution, and 10 ml. of ammonium persulfate solution. Boil for one minute, cool to room temperature, add 10 ml. of 0.05 *N* standard potassium permanganate, precipitate the silver, and titrate with the arsenite-nitrite solution as described above.

An equivalent amount of pure ferrous or ferric sulfate (but not ferrous ammonium sulfate or ferric alum) as free as possible from manganese, may be used instead of electrolytic iron in the standardization. In any case the manganese content of the iron or iron salt added must be determined colorimetrically, preferably with periodate as reagent (*7*, *8*), and a correction applied if necessary.

When the manganese content of the sample falls outside the range 0.3 to 0.8 per cent (using a 1-gram sample) the arsenite-nitrite solution should be standardized against a volume of standard potassium permanganate that contains roughly the same quantity of manganese as the sample. Not more than 15 mg. of manganese may be present in the solution when diluted to 100 ml. previous to titration. In other words, using a 1-gram sample, not more than 1.5 per cent of manganese may be present in the material analyzed if the above directions are to be followed.

Cast irons may be analyzed by the above procedure if the graphite, left after dissolving the sample, is filtered off before the oxidation.

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Determination of Ammoniacal and Urea Nitrogen

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SINCE Marshall (*10*) first published the clinical methods for the determination of urea in urine and blood by means of urease, there have been a number of improvements and modifications made on the technic and apparatus by Van Slyke and his co-workers (*12*, *13*), Fisher (*3*), and Kay and Sheehan (*9*). The latter have worked out a very careful technic for the determination of urea in blood. Fox and Geldard (*5*) modified Marshall's direct titration method for routine chemical analysis. This modified method, however, is not applicable to urea samples that are highly colored or that contain substances which interfere with the end point. For example, ammoniated peat extracts are always highly colored and contain urea, ammonium salts, and under certain conditions a little free ammonia. This investigation was undertaken to modify the urease method so that it can be used in analyzing such samples.

Most of the improvements made on Marshall's method deal with the technic in determining the ammonia liberated by the enzyme action. Since the direct titration method cannot be used, attention is directed to the improvement of the aëration method, which is used in all the modified clinical analyses for urea. The chief objection to this method is the length of time required to make a determination. The ordinary distillation method with sodium hydroxide cannot be employed because the urease preparation used generally contains a certain amount of nitrogen.

The present investigation led to the development of a method whereby ammonia is determined by distillation at 40° C. with an alcoholic solution of an alkali under reduced pressure together with aëration. The urease reaction and distillation are carried out at 40° C., because this temperature is near the optimum point, as demonstrated by Van Slyke and Cullen (*12*), for the enzyme action. Free ammonia or ammonium salts present in the sample can be liberated at this temperature by alkali without any danger of decomposing the urea. The urea is determined in such samples by difference (total ammoniacal and urea nitrogen minus that for free ammonia or ammonium salts). Complete recovery of the ammonia can be accomplished by this method in 10 to 15 minutes.

Apparatus and Procedure

The simple apparatus used is shown in Figure 1.

About 5 cc. of the urea solution or about 50 mg. of the solid sample dissolved in that amount of water are introduced into the reaction flask, *A*, of 100-cc. capacity, which has a constriction and indentations along the upper part to prevent any alkaline spray from being carried over to the absorption vessel, *B*, a 400-cc. cylinder, that contains the necessary amount of 0.1 *N* standard sulfuric acid. A fritted glass plate, *H*, is used as the bubbler. After the reaction flask and the absorption vessel have been connected together and stopcock *C* has been closed, 0.1 gram of urease powder (Arlco-urease) is added to the sample and the reaction flask is placed in the thermostat, *G*, at 40° C. The urease is allowed to react for 15 minutes.

In the meantime the inlet of the reaction flask is connected to an acid bubbler containing dilute sulfuric acid to remove ammonia from the incoming air used for aëration, and the outlet tube, *D*, of the absorption vessel to a water suction pump. It is advisable to place a 2-liter flask between the apparatus and the pump, so that with pinchcock *E* closed, this reservoir can be evacuated while the urease reaction is taking place. At the end of the 15-minute period pinchcock *E* is opened slightly to evacuate the system partially before introducing into the flask, from funnel *F*, 20 cc. of alkaline methyl alcohol solution, each liter of which contains 4 grams of sodium hydroxide and 5 cc. of capryl alcohol. The latter prevents any foaming during distillation. If a larger sample than 5 cc. has been taken, a correspondingly larger amount of alcoholic solution should be used. Air is then admitted into the system at the rate of one bubble per second through the acid bubbler. Slowly the system is further evacuated until the solution boils vigorously, but not violently enough to carry spray over to the absorption vessel, nor to bring the foam in the latter too close to the outlet tube, *D*. Stopcock *C* usually needs to be regulated again at this point in order to maintain the same rate of air flow through the system.

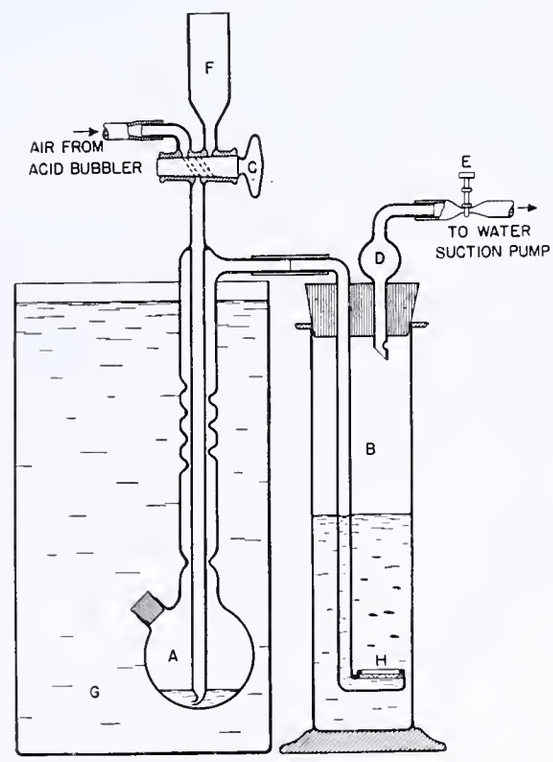

FIGURE 1. DIAGRAM OF APPARATUS

After the first 3 minutes, during which most of the ammonia and alcohol are distilled over, no attention is generally required until the 1.5-minute boiling period is completed. Then more air is admitted and pinchcock *E* closed. After the vacuum has been completely released, the excess acid in the absorption vessel is titrated with standard 0.1 *N* sodium hydroxide, using methyl red as indicator. For very accurate analysis, weaker alkali 0.025 *N* should be used. The carbon dioxide liberated by the enzyme action on the urea has already been removed by the aëration process and can cause no interference with the end point.

For ammonia determinations, the same procedure is followed except that no digestion period is necessary. With a 2-cc. sample, complete recovery of the ammonia can be accomplished by boiling the solution for only 10 minutes.

Blank determinations should be made on each batch of urease powder. The latter is more convenient to use than the urease tablets, which dissolve slowly.

Experimental Results

In order to check the accuracy of this modified method, many attempts were made to prepare urea of very high purity by recrystallizations from water and alcoholic solutions, but a product of about 99.5 per cent purity was usually the result. Other members of this laboratory and Dalman (*1*) have en-

Table I. Comparison of Xanthydrol and Modified Urease Methods

Samples	Urea Found by Modified urease method	Urea Found by Xanthydrol method[a]
	Mg.	*Mg.*
Urea solution A, 2 cc.	32.33	32.29
	32.33	32.32
	32.33	32.35
	Av. 32.33	Av. 32.32
Urea solution B, 2 cc.	34.96	34.93
	34.96	34.90
	34.97	34.96
	34.96	34.90
	Av. 34.96	Av. 34.92
Ammoniated peat extract, 5 cc.	4.02	3.97
	3.99	4.01
	Av. 4.00	Av. 3.99

[a] For best results the weight of xanthydrol used should be fifteen to twenty times that of the urea present.

Table II. Ammoniacal and Urea Nitrogen Determinations

Samples Taken: Ammonium salt solutions		Urea solution	Ordinary Method[a] NH_3 nitrogen	New Method NH_3 nitrogen	New Method Urea nitrogen	NH_3 and Urea Nitrogen
	Cc.	*Cc.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
$(NH_4)_2SO_4$ soln. A	1	...	4.82	4.82	...	...
soln. A	1	...	4.82	4.82	...	...
soln. B	5	...	14.83	14.82	...	...
soln. B	5	...	14.83	14.83	...	...
soln. C	5	...	23.69	23.69	...	...
soln. C	5	...	23.68	23.69	...	...
NH_4NO_3 soln.	5	...	16.17	16.17	...	...
NH_4NO_3 soln.	5	...	16.17	16.17	...	...
...	...	5	...	...	30.08	...
$(NH_4)_2SO_4$ soln. D	2	...	...	9.51	...	...
soln. D	2	...	...	9.51	...	...
soln. D	2	5	...	9.51	...	...
soln. D	2	5	...	9.51	...	...
soln. D	2	5	...	...	30.09[b]	39.60
soln. D	2	5	...	...	30.08[b]	39.59
soln. D	2	5	...	...	30.08[b]	39.59
soln. D	2	5	...	...	30.06[b]	39.57

[a] Distillation with alkali at atmospheric pressure.
[b] Urea nitrogen by difference.

countered similar experiences. Having failed in this, the degree of purity of the urea as determined by the proposed method was compared with that obtained by another analytical procedure. The ordinary Kjeldahl method was found by several members of this laboratory to give inconsistent total nitrogen results for urea, so Fosse's xanthydrol method (*4*) was tried and the results obtained were found to agree with those secured by the urease method, as shown in Table I.

The results for ammoniacal nitrogen determinations were found to agree very closely with those obtained by ordinary distillation with alkali. These, together with the results for urea and ammoniacal nitrogen in the same sample, are tabulated in Table II.

Inactivation of Urease by Heavy Metals

Small amounts of heavy metal salts can inactivate a relatively large amount of enzyme (*2, 11*). Under the conditions employed in the modified method, mercuric and silver ions have about the same toxicity on urease, while cupric ions are not quite so toxic. When such heavy metal ions are present, more urease should be used in order to counteract their effect. Inactivation caused by either mercuric or silver ions can be overcome by a much smaller excess of enzyme than that resulting from cupric ions.

Another method for obtaining accurate results under such conditions is to allow the urease to react for a much longer time. The length of time required to bring about complete decomposition of the urea depends upon the amount and kind of poisons present in the sample. By lengthening the reaction time, accurate determinations can be accomplished in the presence of mercuric and silver ions; with cupric ions present, however, it is much more difficult to obtain good results, and complete decomposition of urea by the urease, even with much longer reaction time, may not be accomplished, although the initial toxic effect is less than that caused by either mercuric or silver ions.

Tables III, IV, and V show the results of experiments demonstrating these points. In these experiments, unless stated otherwise, various amounts of heavy metal salt solutions were added to 2 cc. of urea solution containing 32.24 mg. of urea. Enough water was added, if necessary, to make a total volume of 4 cc. The rest of the experiment was carried out as described in the procedure.

The inactivation of urease by mercuric chloride was observed to vary according to the length of time during which the urea and the mercuric salt are in contact previous to the addition of the enzyme. If this time interval is long enough, the toxic effect disappears almost completely. The length of time necessary for this to occur depends on the amount of the metal salt present. Silver nitrate and cupric sulfate, however, do not show this effect. These results are given in Table VI.

Euler and Svanberg (*2*) noticed a similar effect of mercuric chloride on saccharase. These investigators also found that sucrose exercised a considerable protective action toward inactivation by mercuric ions, while no such action was observed toward the poisoning effect of silver ions on saccharase. In the present experiments, sucrose, it is found, does not give such protective action to the urease toward similar inactivations.

Effects of other salts on the urease reaction were tried in another series of experiments. Urea was completely decomposed by the urease when the stated amounts of each of the following salts were added to a 2-cc. sample containing 32.24 mg. of urea: 0.2 gram of magnesium sulfate heptahydrate, sodium chloride, potassium hydrogen phosphate, or melamine, and 0.1 gram of barium or calcium chloride.

Activity of Urease

The activity of different batches of a commercial urease preparation from jack beans was found to vary greatly. At-

Table III. Inactivation of Urease by Heavy Metals

Heavy Metal Added	Weight of Metal Added	Urea Decomposed
	Mg.	*Av. %*
Mercury (as $HgCl_2$)	0.10	99.6
	0.15	22.0
	0.20	12.2
	0.30	10.8
Silver (as $AgNO_3$)	0.10	98.7
	0.15	22.1
	0.20	13.1
	0.30	11.0
Copper (as $CuSO_4$)	0.10	99.7
	0.15	96.4
	0.20	81.1
	0.30	73.6
	0.50	52.4
	0.70	42.9
	1.00	33.6

Table IV. Effect of Urease on Urea Decomposition in Presence of Heavy Metals

Heavy Metal Added	Weight of Metal Added	Urease Used	Urea Decomposed
	Mg.	*Gram*	*Av. %*
Hg (as $HgCl_2$)	0.20	0.10	12.2
		0.12	22.3
		0.13	55.6
		0.14	99.2
		0.15	100.0
Ag (as $AgNO_3$)	0.15	0.10	22.1
		0.12	78.1
		0.13	99.4
Cu (as $CuSO_4$)	1.0	0.10	33.6
		0.11	47.1
		0.15	63.5
		0.20	92.2
		0.25	96.7
		0.30	100.0

Table V. Effect of Time of Urease Reaction on Urea Decomposition in Presence of Heavy Metals

Heavy Metal Added	Weight of Metal Added	Time of Urease Reaction	Urea Decomposed
	Mg.	*Min.*	*Av. %*
Hg (as $HgCl_2$)	0.15	15	22.0
		30	99.7
Hg (as $HgCl_2$)	0.20	15	12.2
		30	14.1
		45	51.0
		60	99.7
		90	100.0
Hg (as $HgCl_2$)	0.30	90	18.7
		180	100.0
Ag (as $AgNO_3$)	0.15	15	22.1
		30	57.9
		45	77.1
		60	90.5
		70	98.5
		90	100.0
Cu (as $CuSO_4$)	1.0	15	33.6
		30	36.3
		60	43.0
		180	51.8
		240	55.5
		504	96.8

Table VI. Effect of Time Intervals between Addition of Heavy Metals and Urease on Urea Decomposition

Heavy Metal Added	Weight of Metal Added	Time Interval between Addition of Metal and Urease	Urea Decomposed
	Mg.	*Hours*	*Av. %*
Hg (as $HgCl_2$)	0.15	0	22.0
		18	42.8
		67	99.6
Hg (as $HgCl_2$)	0.20	0	12.2
		41	12.4
		162	83.9
		281	99.3
Ag (as $AgNO_3$)	0.15	0	20.8
		67	21.1
Cu (as $CuSO_4$)	1.0	0	33.6
		115	35.7

Table VII. Variations in the Activity of Urease Preparations

Urease Samples	Mercury Added	Urea Decomposed	Remarks
	Mg.	*Av. %*	
3872 A	0	99.7	Bottle of urease tablets prepared, Feb. 15, 1932,[a] in use for about 9 months. Last 5 tablets, dark brown, were powdered and used in these experiments, Jan. 8, 1935
3872 A	0.10	7.7	Hg added as $HgCl_2$
3872	0.10	98.7	Like 3872 A, except bottle was just opened. Light greenish yellow
3965	0.10	9.3	Bottle of urease powder, prepared, Apr. 3, 1933,[a] in use about 4 months
4039	0.10	98.9	Bottle of urease powder, prepared Jan. 22, 1934,[a] opened and used Dec. 11, 1934
4039	0.15	22.0	.....
4071	0.15	99.9	Bottle of urease powder, prepared Oct. 15, 1934,[a] opened and used Jan. 2, 1935
4071	0.20	12.2	.....
4039	0.20	12.1	.....

[a] The dates of preparation were kindly given by the Arlington Chemical Co., Yonkers, N. Y.

mospheric moisture seems to have a deleterious effect on such preparations. The activity of urease from bottles that have been opened and in use for some time was found to have decreased considerably, while a sample of the same batch kept in a dark brown bottle and well sealed for 3 years maintained its activity much better. Results given in Table VII demonstrate these variations in activity of several urease samples.

Discussion

This method has been in use for over a year in this laboratory and has been employed by other members of this bureau for the determination of ammoniacal and urea nitrogen in fertilizer samples. Urea solutions varying in concentration from 1 to 100 mg. of urea per 5-cc. sample have been successfully analyzed.

Van Slyke and Zacharias (*13*) have shown that phosphate buffers of proper concentration can maintain the enzyme action at its maximum, but have also pointed out that the phosphates themselves exert a retarding effect on the action, especially when the urea concentration is low. Kay and Reid (*8*) demonstrated, with buffer solutions of pH values varying from 6.2 to 8.4, that 94 to 96 per cent of the urea can be hydrolyzed, with the maximum at about pH 7. In the presence of small amounts of mercuric and silver salts, according to Jacoby (*7*), urease is more active at values higher than pH 7. In the absence of buffers, the pH of a urea solution after the addition of urease will soon become and remain at about 8.6, which is that of an ammonium carbonate solution. Since with excess of urease, complete decomposition of urea in concentrations as high as 2 per cent can be accomplished under the conditions of the present method, and in this way many unfavorable conditions for the enzyme action may be avoided, such as the presence of small amounts of heavy metal salts, etc., it is convenient to eliminate the use of buffers in routine analysis. Urease powder is now readily obtainable at a reasonable cost and can be kept for a long time under proper conditions.

Mercuric and silver ions have a very similar effect on the activity of urease. Cupric ions, however, seem to react quite differently, although their toxic effect is not as great. It is apparently more permanent. In the presence of cupric salts, a much greater excess of urease is required to counteract the toxic effect, and complete decomposition of urea cannot be brought about readily by prolonging the time of reaction between the enzyme and the urea. In the presence of either mercuric or silver salts, however, this can be accomplished easily. These results are in agreement with those of Hellerman and his co-workers (*6*), who found that urease was not readily poisoned by cupric ions and that hydrogen sulfide could not restore fully the activity of a solution of crystalline urease, which had been partially "extinguished" by cupric sulfate. On the other hand, they showed that the activity of urease, completely "extinguished" by organic mercurials, could be completely or almost completely restored by the action of hydrogen sulfide or potassium cyanide.

Summary

The urease method has been modified so that it can be used to determine urea even in highly colored solution. The accuracy and precision of this modified method are well within the limits required for chemical analysis.

A rapid method for the determination of ammoniacal nitrogen has been developed, whereby ammonia is liberated by distillation at 40° C. with an alkaline alcoholic solution under reduced pressure together with aëration.

Substances interfering with the urease reaction are discussed and means of overcoming their toxic effects are suggested.

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Turbidimetric Determination of Sulfate in Water

Betz-Hellige Method

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A turbidimetric method based on the Tyndall effect for determination of sulfate in water is described. A high degree of accuracy is obtained in relatively low concentrations of sulfates, and by mechanical variations of the instrument four ranges of sulfate are covered: 0 to 5, 0 to 15, 0 to 50, and 0 to 100 parts per million of sulfate. Sulfates in concentrations above 100 parts per million can be determined by diluting sample and multiplying by appropriate factor. Results obtained in this manner checked reasonably well with gravimetric analysis.

TURBIDIMETRIC methods proposed up to the present time for the determination of sulfates depend either upon comparison of the turbidity of one sample with the turbidity of the standard sample or upon the disappearance of a filament of a standard light through a certain depth of the turbid liquid. The method described in this paper is an application of the Tyndall effect for the turbidimetric determination of sulfates.

While this study has been directed on water only, the method can undoubtedly be applied to determination of sulfate in fuel, in cement, and in numerous other fields.

The gravimetric determination of sulfate is admittedly accurate, but is tedious and time-consuming. With very low concentration of sulfates in water, it is necessary to concentrate the sample to obtain an accurate result. Therefore, gravimetric analysis for low sulfate content is inapplicable.

The tetrahydroxyquinone method (*2*) recently proposed offers considerable promise for sulfate concentrations above 80 parts per million. The benzidine hydrochloride titration method is not as accurate as the tetrahydroxyquinone method and cannot be used in low concentrations of sulfate because of the slight solubility of the benzidene sulfate. For a complete review of the literature on sulfate determination the reader is referred to the bibliography recently published by Schroeder (*2*).

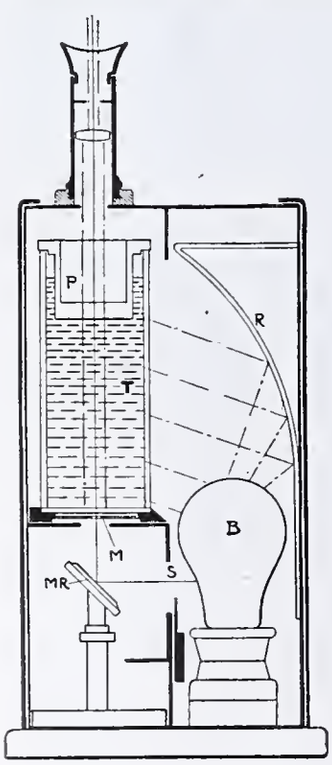

FIGURE 1. DIAGRAM OF TURBIDIMETER

Description of Turbidimeter

The turbidimeter employed in this investigation compares a beam of light with the Tyndall effect produced from a lateral illumination of the specimen by the same light source. As the method involves a comparison of the Tyndall effect on the test liquid itself, the use of standard suspensions and their tedious preparation are entirely overcome, allowing more convenient working, greater simplicity, and greater speed. There is no possibility of error due to the preparation of turbidity standards. The method here described covers a range from 0 to 100 parts per million, to which other methods, such as Burgess-Parr and Jackson, that depend on disappearance of a filament of light in a turbid solution, are not strictly applicable. As far as is known, none of these methods determine sulfate below 50 parts per million and they are questionable in this range. On the basis of these facts, the investigators feel that they are presenting not only a method of excellent accuracy but also a method which covers a range heretofore not covered by other methods.

The apparatus (Figure 1) consists of a metal housing, 17.5 × 12.5 × 40 cm. (7 × 5 × 16 inches) in size. Mounted in the housing is an opal-glass bulb, *B*, a large reflector, *R*, and a precision slit which is operated by a graduated drum knob. At the side of the apparatus to which the door is attached is a platform for the tubes with a mirror, *M*, in a removable frame beneath it, and a circular milk-glass reflector, *MR*, in a metal frame. The rays emanating from the opal-glass bulb are reflected into the liquid column in the tube and by this side illumination of the suspended particles the Tyndall effect is produced. The observation of the Tyndall effect through the ocular on top of the apparatus is facilitated by a silver mirror which rests horizontally beneath the tube. Light rays from the opal-glass bulb also pass through a precision slit and illuminate a circular milk-glass reflector and from there are reflected through a circular aperture in the silver mirror and then through the liquid in the tube into the ocular. These light rays appear to the observer as a circular spot in the center of the Tyndall effect of the illuminated liquid, which is seen lighter or darker than the Tyndall light (Figure 2), depending on the size of the opening of the slit. By revolving the drum knob and thereby adjusting the opening of the slit, the brightness of this spot can be regulated so as to be of the same intensity as the brightness of the surrounding field.

FIGURE 2. OBSERVATION FIELDS

Center, balanced; left and right, unbalanced

The tubes used in this work were made for liquid depth of 10 and 20 mm. The tubes have fused-on plano-parallel bottom plates of optical glass, while the upper end of the filled tube is covered with a short glass plunger with plano-parallel plate which automatically adjusts the proper liquid depth. The same plunger is used with the 20-mm. and 10-mm. tubes.

Different ranges of turbidity can be covered by inserting standard filter plates over the precision slit and these plates will be designated as gray-glass, milk-glass, and clear.

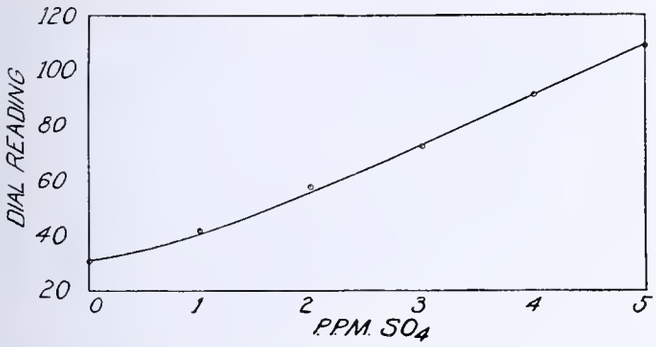

FIGURE 3. TURBIDIMETER CALIBRATION

Range 1, 0 to 5 p. p. m. of sulfate. Gray filter, 20-mm. cell, 50-cc. sample

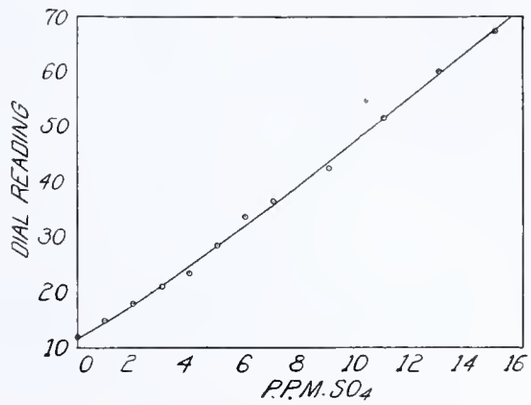

FIGURE 4. TURBIDIMETER CALIBRATION

Range 2, 0 to 15 p. p. m. of sulfate. Milk filter, 20-mm. cell, 50-cc. sample

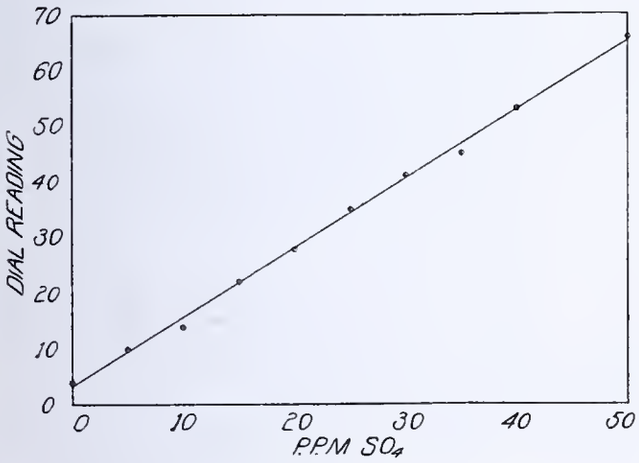

FIGURE 5. TURBIDIMETER CALIBRATION

Range 3, 0 to 50 p. p. m. of sulfate. Clear filter, 20-mm. cell, 50-cc. sample

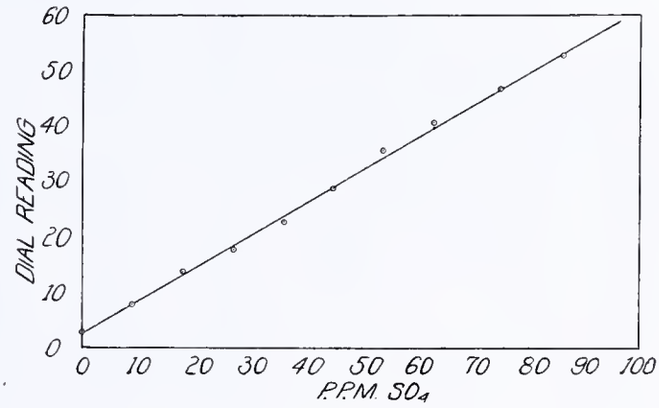

FIGURE 6. TURBIDIMETER CALIBRATION

Range 4, 0 to 100 p. p. m. of sulfate. Clear filter, 10-mm. cell, 25-cc. sample

Procedure

REAGENTS. Standard salt-acid solution, 240 grams of sodium chloride plus 20 cc. of hydrochloric acid (sp. gr. 1.19) per liter. This solution must be filtered until a zero turbidity is obtained. Barium chloride ($BaCl_2.2H_2O$), 20- to 30-mesh crystals.

METHOD. If the sulfate content is below 50 parts per million a 50-cc. sample is taken and the test made in the 20-mm. cell. With a 50-cc. sample, 10 cc. of the standard salt-acid solution are added. If the sample contains between 50 and 100 parts per million of sulfate, a 25-cc. sample is taken in a 10-mm. cell and 5 cc. of salt-acid solution are added. To the sample is added 0.29 gram of 20- to 30-mesh barium chloride crystals measured by a standardized cup. The solution is stirred for exactly 1 minute, the plunger tube inserted, and readings are taken 4 to 6 minutes after the precipitation. An average of two readings is taken and the reading obtained compared with values from the standard curve to obtain the sulfate content of the sample. An initially turbid solution must either be filtered or a blank reading made, in terms of sulfate, before the precipitation of the barium sulfate.

Discussion

Standard curves were prepared by taking a given volume of standard sodium sulfate solution, diluting to desired volume, and obtaining the reading. The cup used for measuring the barium chloride crystals was found to have a maximum variation in measurement of the crystals of 3.5 per cent; such variation made no difference in the reading obtained, as the quantity of barium chloride was always in considerable excess of that necessary to precipitate all the sulfate present. It is well, however, to standardize on the amount of barium chloride used, as large variations may affect the turbidity produced. Parr (*1*) suggested the use of 20- to 30-mesh barium chloride crystals for turbidimetric work. The size of the crystals has been investigated by others and this standard was arbitrarily accepted for use in this work. The salt-acid concentration employed is the same as that proposed by Parr and has been checked by Schroeder (private communication). The bulb in the instrument is a standardized bulb and the instrument is furnished with a duplicate bulb of exactly the same power, eliminating error due to a possible variation in light source.

The values obtained for the lowest range, 0 to 5 parts per million, are presented in Figure 3. They were obtained by employing a standard sodium sulfate solution containing 0.01 mg. of sulfate per cc. with the gray filter and the 20-mm. cell. This solution, as well as the other sulfate solutions used in calibration, was prepared by dilution from a solution standardized gravimetrically.

For the preparation of Figure 4, covering a range 0 to 15 parts per million of sulfate, a solution of sodium sulfate containing 0.01 mg. of sulfate per cc. was used for the lower values and another solution containing 0.025 mg. of sulfate per cc. for the higher values. For this range the milk filter and the 20-mm. cell were employed.

For the range from 0 to 50 parts per million of sulfate (Figure 5), a standard sodium sulfate solution containing 0.05 mg. of sulfate per cc. was used. The clear filter and 20-mm. cell were used for this range.

For the range from 0 to 100 parts per million (Figure 6), which was obtained by use of the 10-mm. cell and clear filter, a standard sodium sulfate solution containing 0.075 mg. per cc. and another containing 0.107 mg. per cc. were employed.

The effects of Ca^{++}, Mg^{++}, Fe^{+++}, Al^{+++}, PO_4^{---}, and SiO_3^{--} were studied and are presented in Table I. No appreciable interference was noticed. The color of the iron

TABLE I. EFFECT OF INDIVIDUAL IONS

Dial Reading	Sulfate Present	Sulfate Found	Ion Present	Sulfate Variation Found	Sulfate Tolerance Allowed	Range
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	
			Ca			
65	2.5	2.6	40	0.1	0.1	1
38	7.5	7.6	62	0.1	0.3	2
22	15	15	206	0.0	0.8	3
47	35	35	206	0.0	2.6	3
22	30	32	412	2.0	1.7	4
43	65	64	412	1.0	3.5	4
			Mg			
63	2.5	2.4	24	0.1	0.1	1
37	7.5	7.3	30	0.2	0.3	2
22	15	15	96	0.0	0.8	3
44	30	33	96	3.0	2.6	3
22	30	32	180	2.0	1.7	4
34	56	52	180	4.0	3.5	4
			SiO_3			
62	2.5	2.4	2.5	0.1	0.1	1
37	7.5	7.3	5.0	0.2	0.3	2
22	15	15	7.5	0.0	0.8	3
46	35	34.5	7.5	0.5	2.6	3
22	30	32	10	2.0	1.7	4
46	68	72	15	4.0	3.5	4
			Fe			
85	2.5	2.4	2.4	0.1	0.1	1
38	7.5	7.6	2.4	0.1	0.3	2
22	15	15	4.8	0.0	0.8	3
47	35	34.5	4.8	0.5	2.6	3
24	30	31	9.6	1.0	1.7	4
43	64	68	16	4.0	3.5	4
			Al			
63	2.5	2.4	1.0	0.1	0.1	1
37.5	7.5	7.5	2.0	0.0	0.3	2
22	15	15	5.5	0.0	0.8	3
49	37.5	36.5	5.5	1.0	2.6	3
22	30	32	10.8	2.0	1.7	4
40	64	62	15.6	2.0	3.5	4
			PO_4			
63.5	2.5	2.5	2.2	0.0	0.1	1
37.5	7.5	7.5	5.5	0.0	0.3	2
23	15	16	11	1.0	0.8	3
46	37.5	34.5	11	3.0	2.6	3
47	37.5	35	11	2.5	2.6	3
22	30	32	16.5	2.0	1.7	4
41	64	63	26.4	1.0	3.5	4
42	64	66	26.4	2.0	3.5	4

TABLE II. EFFECT OF MIXTURES OF IONS

Dial Reading	Sulfate Present	Sulfate Found	Ion Present			Sulfate Variation Found	Sulfate Tolerance Allowed	Range
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	
			Ca	Fe	SiO_3			
38.5	7.5	7.8	103	2.0	10	0.3	0.3	2
42	32	31	103	5.0	10	1.0	2.6	3
			Al	PO_4				
17	24	24.5	10	20	..	0.5	2.6	4
35	56	54	10	20	..	2.0	3.5	3
			Ca	PO_4				
36	7.5	7.0	17	10	..	0.5	0.3	2
40	30	29.5	103	24	..	0.5	2.6	3
			Mg	SiO_3				
111	5.0	5.1	60	10	..	0.1	0.1	1
55	40	41.5	60	10	..	1.5	2.6	3

solutions was taken into consideration by running a blank on the unprecipitated solution.

Mixtures of several of these ions were made to give synthetic solutions, the following mixtures being tested: Al^{+++} and PO_4^{---}; Ca^{++} and PO_4^{---}; Ca^{++}, Fe^{+++}, and SiO_3^{--}; Mg^{++} and SiO_3^{--}. Table II embodies these data. An examination will show that mixtures also had no effect on the method. Color of iron solutions was corrected as already stated.

As a final test of the applicability of the method, a number of samples of raw water were taken, together with a number of boiler water samples, and results compared with gravimetric determinations of the sulfate content. These values, presented in Table III, show good agreement. In the majority of cases the gravimetric results were higher than those obtained by the Betz-Hellige method. This is explained by the adsorption of the interfering ions by the barium sulfate precipitate. A comprehensive discussion of adsorption by barium sulfate is given by Treadwell and Hall (*3*). The investigators point out that within the range of the method (0 to 100 p. p. m. of sulfate) the results obtained with the Betz-Hellige method agree with gravimetric within the tolerance expected. Above 100 p. p. m. fair agreement was obtained. These variations are easily understood when it is considered that factors as high as 50 were employed, so that any error taken in the reading corresponds to 50 times that error in the final sulfate content recorded. Column 8 in Table III (zero point) represents the dial reading, equivalent to turbidity in terms of sulfate, obtained on the unprecipitated sample. This had to be done in a few samples, as their turbidity could not be removed by filtration. Column 9 (factor) represents the number used to obtain the sulfate when a diluted sample is employed, and is the relation between the amount of sample used and 50 cc. Thus, if 5 cc. of a solution were diluted to 50 cc., the sulfate obtained would be multiplied by 10.

TABLE III. COMPARATIVE RESULTS OF TURBIDIMETRIC AND GRAVIMETRIC ANALYSIS ON ACTUAL WATER SAMPLES

Sample	Dial Reading	Sulfate: Turbidimetric	Sulfate: Gravimetric	Difference	Tolerance Allowed	Range	Zero Point	Factor
		P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*			
1	25	1.3	0.7	0.6	0.5	2	20.5	..
	85.5	1.2	0.7	0.5	0.1	1	65	..
2	71	13.9	13.2	0.7	0.5	2	14	..
	20	13.0	13.2	0.2	0.8	3	Normal	..
3	47	35	32.5	2.5	2.6	3	Normal	..
	25	34	32.5	1.5	1.7	4	Normal	..
4	27	88	93	5.0	3.5	4	Normal	2.5
	28	97	93	4.0	2.6	3	Normal	5.0
5a	29	450	483	33	...	4	Normal	10.0
5b	41	320	324	4	...	4	Normal	5.0
	23	340	324	16	...	4	Normal	10.0
6a	35	1350	1348	2	...	4	Normal	25.0
	33	1225	1348	123	...	3	Normal	50.0
6b	45	1750	2044	294	...	4	Normal	25.0
	48	1850	2044	194	...	3	Normal	50.0

TABLE IV. ANALYSIS OF SOLUTIONS USED

Sample	Analysis: Total hardness	HCO_3^-	CO_3^-	OH^-	Cl^-	pH
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	
1	20	8	0	0	4	6.5
2	50	30	0	0	8	6.9
3	65	14	0	0	10	6.7
4	88	48	0	0	16	6.9
5a	60	0	168	88	208	11.1
5b	48	36	184	0	98	10.3
6a	0	0	260	884	236	11.6
6b	50	0	132	166	224	11.6

TABLE V. LIMITS OF ACCURACY OF BETZ-HELLIGE METHOD FOR SULFATES

Sulfate Range	Part of Range Where Accuracy Was Determined	Average Accuracy
P. p. m.		*P. p. m.*
0–5	Center	0.1
0–15	Lower	0.2
0–15	Upper	0.5
0–50	Lower	0.8
0–50	Upper	2.6
0–100	Lower	1.7
0–100	Upper	3.5

The effect of temperature was studied and no appreciable variation found between 17° and 32° C. Different lots of barium chloride crystals were tested to see if any variation would be introduced, but none was found.

It was thought that different operators would read the instrument differently. Accordingly, six inexperienced operators were tested on a number of standard solutions in order to obtain the limit of the operator's tolerance that might be

normally expected. In Table V are given the average limits of accuracy which were obtained from an average of the results on the different portions of each range. On range 1 (in the central portion) the six operators varied from 0 to 0.1 p. p. m. of sulfate. In the lower portion of range 2, they varied from 0.1 to 0.2 p. p. m. of sulfate and in the upper, from 0.4 to 0.7 p. p. m. of sulfate. For higher sulfate content, covered by ranges 3 and 4, the following variations were incurred: in the lower portion of range 3, from 0 to 2.0 p. p. m. and in the upper from 1 to 5 p. p. m.; in the lower region of range 4 from 0.5 to 4 p. p. m. and in the upper 1.0 to 6 p. p. m.

Conclusions

The results obtained with this method compared favorably with those obtained by gravimetric analysis.

None of the ions or mixtures of ions, with the exception of iron, exerted any appreciable influence on the method. This influence of iron was due to color and was corrected by running a blank on the unprecipitated sample.

A variation in temperature between 17° and 32° C. had no effect on the determination. Different batches of the precipitating agent, $BaCl_2.2H_2O$, also were found to exert no determining influence on the method.

Sulfate concentrations above the direct range of the instrument can be obtained by diluting the sample and multiplying by the appropriate factor.

The method is rapid, a determination taking less than 10 minutes, and strictly applicable to boiler and feed-water studies where accurate low sulfate determinations are desirable. The investigators feel that there is a possible application in other fields for sulfate determination.

Acknowledgment

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Determination of Lead

A Modification of the Fischer-Leopoldi Method

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A colorimetric method based on the use of dithizone (diphenylthiocarbazone) for the microdetermination of lead is described. The lead is extracted from solution by means of a chloroform solution of dithizone, the intensity of the resultant red color of the lead dithizone compound in chloroform solution is measured, and the corresponding quantity of lead is read from a curve constructed from measurements made on known amounts of lead.

The method is applicable to the estimation of lead in spray residues and biological materials and is sensitive to approximately 0.001 mg. in these materials. Slight modifications of the method permit determination of lead in the presence of the interfering elements, bismuth and stannous tin.

The method has the advantage of being both extremely sensitive and relatively rapid. With spray residues as many as 36 determinations may be made in one day, and with biological materials approximately 20, depending upon the type of material and method of preparing samples for analysis.

THE recent regulatory measures of the United States Food and Drug Administration limit the amount of lead that may be present in spray residues on fruit, and necessitate the development of methods which are capable of determining minute quantities of lead and which at the same time are less cumbersome and time-consuming than those hitherto available. Within the past 2 years a number of methods have been proposed to fill this need, including a colorimetric sulfide method by Wichmann and Vorhes (*6*), an electrolytic method by Wichmann and Clifford (*5*), a colorimetric dithizone method by Vorhes and Clifford (*4*) based on the method of Fischer and Leopoldi (*2*), and a photometric method by Samuel and Shockey (*3*).

In an attempt to use the dithizone (diphenylthiocarbazone) colorimetric method for lead in the routine examination of spray residues, difficulties were encountered and a different modification of the Fischer-Leopoldi method was developed and has been used for the past two seasons in the analysis of the residue on nearly a thousand samples of apples. It is the purpose of this paper to describe the method.

The Fischer-Leopoldi (*2*) method is based on the following properties of dithizone (*1*):

1. Dithizone is insoluble in water or dilute acid but very soluble in chloroform or carbon tetrachloride, giving a green color to the solution.
2. A dilute ammoniacal solution dissolves dithizone and extracts it from the chloroform or carbon tetrachloride, giving a brownish color to the aqueous solution.
3. Ammonium citrate decreases the solubility of dithizone in a dilute ammoniacal solution.
4. Lead salts in aqueous solution when shaken with dithizone dissolved in chloroform or carbon tetrachloride react with the dithizone to form a highly colored cherry-red compound soluble in chloroform. This lead dithizone compound is not extracted from chloroform or carbon tetrachloride by dilute ammonium hydroxide. A dilute acid solution, however, decomposes the

lead dithizone compound and extracts the lead but leaves the free dithizone quantitatively in the chloroform or carbon tetrachloride.

Fischer and Leopoldi extracted the lead in the presence of potassium cyanide with two or three portions of carbon tetrachloride–dithizone solution and removed the excess of dithizone by means of two or three extractions with dilute ammonia. Then with dilute acid they decomposed the lead dithizone compound, thereby removing the lead from the carbon tetrachloride and leaving the free dithizone quantitatively in the carbon tetrachloride. The green dithizone–carbon tetrachloride solution was made to volume with carbon tetrachloride and compared colorimetrically with a standard prepared in an identical manner as the sample. They state that the dithizone solution must be fresh; that the presence of lead causes the color to change from green to red almost instantly; that a curve which shows the relation between the quantity of lead extracted and the intensity of the green color produced after the lead dithizone compound has been decomposed is linear; that in the presence of potassium cyanide the only heavy metals that interfere with the reaction are stannous tin, thallium, and bismuth; that a quantity of lead as small as 0.0001 mg. in a drop of solution can be detected; and that their experimental error was 3 to 5 per cent when determining lead present in the amount of 0.01 per cent and 5 to 8 per cent in amounts less than 0.001 per cent.

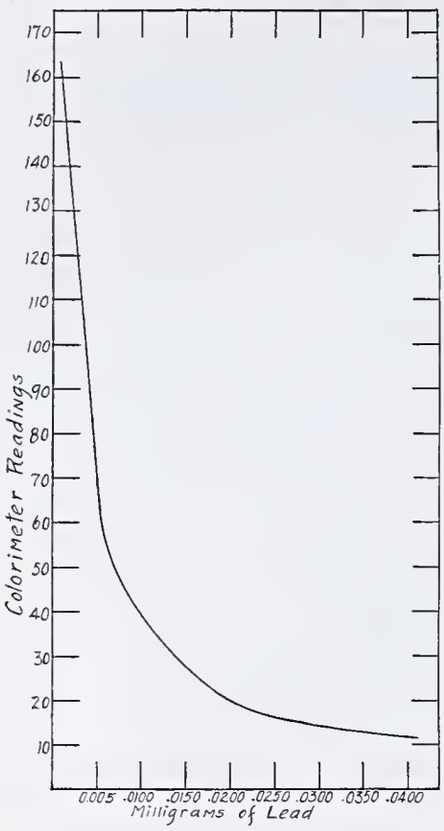

Figure 1. Curve Relating Colorimeter Readings to Milligrams of Lead

In the authors' study of the underlying principles of the Fischer-Leopoldi method it was found that a much shorter procedure could be used without the sacrifice of accuracy, and even with greater accuracy and fewer possible sources of error. Contrary to finding a linear relationship between the intensity of the green color of the dithizone and the lead content, the authors found that the relationship between the intensity of the red color of the lead dithizone solution and the lead content was not linear, but could nevertheless be advantageously used for the colorimetric determination of the amount of lead present. In the first place this eliminated the step of decomposing the lead dithizone and removing the lead, which saved considerable time and possibility of error in manipulation, and furthermore the red color is more easily compared in the colorimeter and is more stable than the green color of the dithizone itself. In some cases the red dithizone lead standards have been found to be unchanged after more than a month and the chloroform dithizone solution reagent requires no other precaution for its preservation than the customary brown-glass container used for the chloroform itself. Sufficient reagent was usually prepared for 3 or 4 weeks' use. It has also been found unnecessary in this procedure to purify the dithizone powder before making up the reagent. The dithizone used was procured from Eastman and from two other independent sources. Further saving of time was effected when it was found that with proper precautions one extraction of the sample for the removal of lead gave as good results as when two or three extractions were made, and only two extractions were ordinarily necessary for the removal of the excess dithizone.

Reagents

Solution A. Chloroform, c. p.

Solution B. Ammonium citrate, 5 per cent solution prepared from citric acid by making slightly alkaline with ammonium hydroxide.

Solution C. Potassium cyanide, 5 per cent solution.

Solution D. Dithizone, 10 mg. dissolved in 400 cc. of chloroform.

Solution E. (Lead-free reagent 1). Add 30 cc. of solution C, 15 cc. of B, and 5 cc. of concentrated ammonium hydroxide to approximately 450 cc. of distilled water.

Solution F. (Lead-free reagent 2). Add 10 cc. of solution C and 5 cc. of concentrated ammonium hydroxide to about 500 cc. of distilled water.

Solution G. (Standard lead solution). Dissolve 1.5985 grams of recrystallized lead nitrate in 100 cc. of 0.1 per cent nitric acid (1 cc. = 0.01 gram of lead). Dilute 0.5 cc. of this solution to 500 cc. (1 cc. = 0.01 mg. of lead).

Solutions E and F should be tested for the absence of lead as follows:

Place 20 cc. in a small separatory funnel, add 1 cc. of dithizone and 5 cc. of chloroform, shake, separate, and extract the chloroform layer once or twice with another 20 cc. of the solution. The final chloroform layer should be colorless or very faintly red. (The faint red may persist if separatory funnels made from ordinary glass are used. A correction for this minute amount of lead, however, is included in the blank which must always be run on the reagents used in the preparation of the sample for analysis.)

If solutions E and F are not free from lead, they should be treated as follows:

To solution E add a few cubic centimeters of dithizone (solution D) and about 15 cc. of chloroform and shake vigorously for 5 minutes. Allow at least 5 minutes for the layers to separate. If the chloroform layer is red and the water layer colorless, add more dithizone and repeat the shaking and the separation. Draw off the chloroform layer. Repeat the above procedure, adding about 1 cc. of dithizone and 10 cc. of chloroform each time until the chloroform layer is practically colorless or slightly green. This layer should become colorless or very faintly red when extracted once or twice with solution F. For solution F proceed as in the preparation of solution E. (In this solution, no more dithizone should be added than is necessary to remove all the lead. The water layer should have only a slightly brownish color immediately after preparation and should become entirely colorless after standing several hours. The solution should not be used until it is colorless.) The brown color may also be removed by shaking out with 0.25 gram of ash-free decolorizing charcoal, thus avoiding the necessity of waiting for the solution to decolorize. If charcoal is used, it is not necessary to avoid the addition of an excess of dithizone.

Procedure

Extraction of Lead from Sample. Place approximately 15 cc. of solution in a 150-cc. Squibb separatory funnel and add a neutralized aliquot of the sample. From a buret add a sufficient amount of dithizone solution in 1-cc. portions so that, after a few vigorous shakings and allowing the layers to separate for a few seconds, the lower layer has a noticeable purple color, indicating the presence of an excess of dithizone. Add chloroform (also from a buret) to make a total volume of dithizone and chloroform exactly 10 cc. Shake and allow the layers to separate. Give the funnel an occasional slight swirling motion and a gentle horizontal shaking while the layers are separating, in order to cause the drops of chloroform which collect at the top of the aqueous layer to fall to the bottom. Draw off the chloroform layer into a second separatory funnel in which 20 cc. of

solution F have been placed. Discard the solution remaining in the first funnel.

Extraction of Excess Dithizone from Chloroform Layer. Shake the second separatory funnel and allow the layers to separate as before. Separate and repeat the extraction and separation (occasionally a third extraction is necessary) with 20 cc. of solution F until the upper solution is practically colorless, indicating that the dithizone has all been removed.

Preparation of Lead Dithizone Solution for Reading in Colorimeter. Open the stopcock of the separatory funnel slightly until the chloroform replaces the water in the bore; then by means of a cotton swab remove the moisture from the stem of the funnel. Draw off the clear or slightly turbid chloroform layer into a dry test tube, retaining in the separatory funnel any small amount of emulsion which may have formed and collected at the chloroform-water interface. (Since the dithizone solution and the chloroform are measured accurately from burets and the amount of chloroform retained in the water layer when running the sample undoubtedly is approximately equal to that in the standard, and since any chloroform which forms an emulsion with the water presumably retains a proportional amount of lead, no chloroform should be added to correct any loss in the volume of the finished sample. The small amount of emulsion which sometimes persists should, therefore, be retained in the funnel.) Stopper the test tube and, if necessary, allow it to stand for several hours for cloudiness to disappear. Cloudiness is sometimes due to the formation of a fine emulsion of aqueous solution in the chloroform during the shaking, which may persist for some little time. It also appears when the chloroform solution cools below the temperature at which the separation occurs. In the latter case it may be removed by warming the solution very slightly by holding the test tube in the palm of the hand. Compare in a colorimeter with a standard. The standards are prepared in a similar manner as the unknown. Since the intensity of the color is not directly proportional to the lead content, it is necessary to make up a series of standards and plot a curve from which to read the quantity of lead present.

Construction of Graph. In order to construct a standard curve, determinations were made on four series of standard lead solutions. Each series consisted of ten samples containing 0.0010, 0.0025, 0.0050, 0.0100, 0.0150, 0.0200, 0.0250, 0.0300, 0.0350, and 0.0400 mg. of lead, respectively, and each was read against 0.0200 mg. of lead as the standard. (When an extremely small amount of lead is to be determined, a curve should be plotted with 0.0500 mg. of lead as the standard.) The colorimeter readings were made with the standard set at 20, or when this was not practical they were calculated to this value.

The results are shown in Table I, which gives the amount of lead present in the solution, the corresponding colorimeter readings, and the averages of these readings. Figure 1 shows the averages of the readings in Table I expressed in the form of a graph. Once this graph has been constructed it may be used indefinitely, but the 0.0200 standard is made up daily in routine work.

Table I. Relation between Quantity of Lead Present and Colorimeter Readings

Lead Present	Colorimeter Readings				
	Series 1	Series 2	Series 3	Series 4	Average
Mg.					
0.0010	160	165	155	...	160
0.0025	120	117	119	121	119
0.0050	67.8	69.0	69.2	68.4	68.8
0.0100	38.2	38.0	38.6	38.2	38.2
0.0150	25.2	26.4	26.8	26.0	26.1
0.0200	20.0	20.0	20.0	20.0	20.0
0.0250	16.4	16.8	16.9	16.5	16.7
0.0300	14.5	14.8	15.0	14.6	14.7
0.0350	13.1	13.3	13.0	12.9	13.1
0.0400	11.8	12.2	12.1	12.2	12.1

Accuracy of the Method. Determinations were made on a large number of solutions containing known amounts of lead added as lead nitrate in order to determine the accuracy of the method. In Table II are presented the results of a number of representative analyses, showing the colorimeter readings, the amount of lead present, the amount found by analysis, and the percentage error. With only ordinary care the maximum error can be kept below 5 per cent. By the exercise of greater care and attention to details, such as choosing the size of the sample to be analyzed so that the colorimeter readings fall on the most sensitive part of the curve, the use of Pyrex separatory funnels, double-distilled water of very low lead content, etc., it should be possible to increase the accuracy still further. Since the method is extremely sensitive, it is essential that precautions be taken to eliminate all sources of contamination of lead. All glassware should be cleaned with nitric acid before use, and reagents with the smallest possible quantitites of lead in them should be selected. Stopcocks should be lubricated with lead-free lubricants; a pure white vaseline was found satisfactory for this purpose.

Table II. Results of Determinations on Solutions of Known Lead Content

Colorimeter Readings	Lead Present	Lead Found	Error	
	Mg.	*Mg.*	*Mg.*	%
54.5	0.0070	0.0067	−0.0003	−4.3
44.0	0.0080	0.0084	+0.0004	+5.0
32.8	0.0120	0.0120	0.0000	0.0
32.5	0.0125	0.0120	−0.0005	−4.0
32.6	0.0125	0.0121	−0.0004	−3.2
29.0	0.0135	0.0134	−0.0001	−0.7
23.8	0.0165	0.0167	+0.0002	+1.2
23.7	0.0175	0.0169	−0.0006	−3.5
23.7	0.0175	0.0169	−0.0006	−3.5
17.8	0.0225	0.0228	+0.0003	+1.3
16.8	0.0250	0.0250	0.0000	0.0

Procedure for Routine Work. When making a large number of determinations it is advantageous to run at least six samples simultaneously. An adjustable rack holding twelve separatory funnels (Figure 2) was found very convenient for this purpose. The following procedure works to good advantage:

Place 15 cc. of solution E in each of the six separatory funnels in the lower row. Add a neutralized aliquot of the sample and mix. (If a large number of samples are to be analyzed—as, for example, spray residue solutions in which the acidity of the samples is fairly uniform—solution E should be made up with sufficient ammonium hydroxide so that the quantity of ammonium hydroxide in 15 cc. is slightly in excess of that necessary to neutralize the acid in a 5-cc. sample. This eliminates the necessity of neutralizing each individual sample or of adding ammonium hydroxide to solution E in each separatory funnel.)

Add the dithizone and chloroform to each of the funnels, as directed under "Extraction of lead from sample," and shake. Place 20 cc. of solution F in each funnel in the upper row. Draw off the chloroform layer from the first funnel into the funnel directly above and discard the remaining water layer. Shake the upper funnel. Proceed in the same way with each of the other five funnels. Place 20 cc. of solution F in each of the lower row of funnels and proceed as before. (If the proper amount of dithizone has been added, two extractions will be sufficient to remove the excess of dithizone and the water layer will be practically colorless; if not, another extraction will be necessary.) Remove the water from the stems of the separatory funnels by means of a cotton swab. Draw off the chloroform layers into test tubes and stopper the tubes. The solutions are now ready to be read in the colorimeter.

Factors Influencing Rapidity and Accuracy of Method

Satisfactory methods in control work must necessarily require as little time as possible for their manipulation, sometimes at the sacrifice of extreme accuracy. Therefore in order to make the procedure as short as possible and maintain the desired accuracy, it appeared necessary to study and determine the following: (1) the number of extractions necessary to remove all the lead from the sample; (2) the quantity of dithizone necessary to extract all the lead from the sample (this is important because if a large excess is added extra washings are necessary for its removal); (3) the time required for shaking in each extractive operation; (4) the number of extractions necessary to remove the excess of dithizone from the chloroform layer; (5) the possibility of error due to solubility of the lead dithizone compound in the

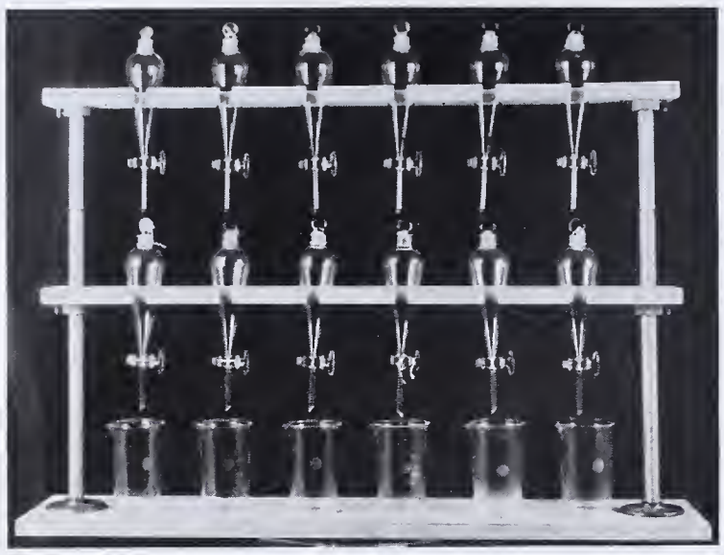

FIGURE 2. ADJUSTABLE RACK FOR SEPARATORY FUNNELS

ammoniacal solution; and (6) the quantity of solvent lost by volatilization or solubility and the effect of this loss on the accuracy of the method.

To determine the number of extractions necessary to remove all the lead from the sample, each of a number of solutions of known lead content was extracted three times with an excess of dithizone and chloroform. The quantity of lead found in each extraction is shown in Table III.

TABLE III. LEAD REMOVED BY SUCCESSIVE EXTRACTIONS WITH DITHIZONE

Lead Present	Lead Found: First extraction	Second extraction	Third extraction
Mg.	*Mg.*	*Mg.*	*Mg.*
0.0050	0.0052	0.0002	0.0000
0.0100	0.0100	0.0002	0.0001
0.0200	0.0195	0.0003	0.0000
0.0250	0.0238	0.0005	0.0001
0.0300	0.0285	0.0007	0.0002
0.0350	0.0350	0.0003	0.0001
0.0400	0.0400	0.0001	0.0000

Although the data in Table III do not take into consideration the solubility of lead dithizone in solution F, they show that only a small amount of lead was recovered after the first extraction of the sample and that only one extraction of the sample with the dithizone-chloroform solution is necessary.

In order to determine the quantity of dithizone necessary to extract all the lead from solution, a number of synthetic lead solutions were extracted with different quantities of dithizone-chloroform reagent. The color of the chloroform layer was taken as the criterion for determining the quantity of dithizone needed. Such quantities of dithizone were taken that, after the extraction, the color of the chloroform layers varied from pure red through different combinations of red and green to a large excess of green. The results indicated clearly that when sufficient dithizone was added so that, after shaking, the chloroform layer showed positive evidence of green mixed with the red giving rise to a reddish purple, practically no lead remained in the aqueous solution.

Experience has shown that a thorough shaking of each sample for 15 seconds is sufficient time for each extraction of the lead from the sample and for each extraction for the removal of the excess dithizone from the chloroform layer.

The excess dithizone in the chloroform layer which does not combine with the lead must be removed completely. This is accomplished by extracting the chloroform layer two or three times with the ammoniacal solution F until the ammoniacal layer remains colorless. If the excess of dithizone in extracting the lead from the sample is kept low, two extractions of approximately 20 cc. each are sufficient.

The possibility of error due to the solubility of the lead dithizone compound in solution F under the conditions of the extraction was determined by reëxtracting the lead dithizone–chloroform layer, after it was ready for the colorimeter reading, with two additional 20-cc. portions of ammoniacal solution F, and taking the colorimeter reading after each extraction. These results are shown in Table IV.

TABLE IV. LEAD REMOVED BY ADDITIONAL EXTRACTIONS WITH SOLUTION F

Lead Present	Lead Found: After second extraction	After first additional extraction	After second additional extraction
Mg.	*Mg.*	*Mg.*	*Mg.*
0.005	0.0047	0.0044	0.0040
0.005	0.0044	0.0042	0.0039
0.0100	0.0099	0.0091	0.0069
0.0100	0.0095	0.0092	0.0082
0.0150	0.0147	0.0139	0.0134
0.0150	0.0158	0.0143	0.0136
0.0200	0.0204	0.0204	0.0194
0.0200	0.0200	0.0204	0.0200
0.0250	0.0255	0.0250	0.0240
0.0250	0.0250	0.0250	0.0240
0.0300	0.0290	0.0290	0.0275
0.0300	0.0305	0.0290	0.0285

The data in Table IV show that lead dithizone is appreciably soluble in solution F and no more extractions should be made than necessary to remove the excess dithizone. This emphasizes the fact that the volume of the solution from which the lead is to be extracted and also the volume and number of the wash solutions must be kept as uniform as possible. If the above precautions are taken, however, with both the samples and the standard, no serious error results from the solubility factor.

The quantity of solvent lost during the procedure of a determination, except where an appreciable amount of emulsion is formed and discarded, is approximately 0.4 cc. This loss, however, is the same in both the standard and the samples, and again there appears to be no considerable source of error here.

TABLE V. COMPARISON OF RESULTS OF LEAD DETERMINATIONS BY "LONG" AND "SHORT" PROCEDURES

Analyst	Sample	Lead Present	Lead Found by Long Method	Error	Lead Found by Short Method	Error
		Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
A	1	0.0050	0.0050	0.0000	0.0049	−0.0001
	2	0.0100	0.0098	−0.0002	0.0094	−0.0006
	3	0.0150	0.0148	−0.0002	0.0147	−0.0003
	4	0.0200	0.0200	0.0000	0.0200	0.0000
	5	0.0300	0.0300	0.0000	0.0300	0.0000
B	6	0.0070	0.0073	−0.0003	0.0072	+0.0002
	7	0.0120	0.0118	−0.0002	0.0118	−0.0002
	8	0.0200	0.0200	0.0000	0.0200	0.0000
	9	0.0220	0.0218	−0.0002	0.0228	+0.0008
	10	0.0270	0.0263	−0.0007	0.0266	+0.0004
	11	0.0320	0.0324	−0.0004	0.0320	0.0000

For the purpose of comparing the accuracy of the procedure described earlier in this paper with that in which more extractions are made, several series of known lead solutions were analyzed by making two extractions of the samples with dithizone and three extractions for the removal of the excess dithizone, and a standard curve was plotted. A number of known solutions were then run by both procedures. Table V gives a comparison of the results by the above procedure ("long") with those by the procedure described earlier in this paper ("short"), made by two different analysts. These data indicate that the results by the "short" method are comparable with those by the "long" method.

From the preceding studies it appears that one extraction

with a slight excess of dithizone is sufficient for the removal of the lead from the sample, and that two extractions are sufficient for the removal of the excess dithizone from the chloroform layer, provided the proper amount of dithizone is used for extraction of the lead.

TABLE VI. EFFECT OF INCREASING THE CONCENTRATION OF AMMONIUM HYDROXIDE IN SOLUTIONS E AND F

Lead Present	Lead Found 1[a]	Lead Found 2[b]
Mg.	*Mg.*	*Mg.*
0.0200	0.0199	0.0196
0.0200	0.0200	0.0184
		0.0200
		0.0200
0.0200	0.0206	0.0206
0.0200	0.0204	0.0210

[a] Solutions E and F containing 5 cc. of NH_4OH per 500 cc. of solution.
[b] Solutions E and F containing 15 cc. of NH_4OH per 500 cc. of solution.

In order to show the effect of increasing the ammonium hydroxide concentration of the solution from which the lead is extracted and of the solution used for extracting the excess dithizone (solutions E and F), lead determinations were made on known solutions using solutions E and F, and also using solutions E and F to each of which had been added an extra 10 cc. of concentrated ammonium hydroxide per 500 cc. of solution. The results of these determinations are shown in Table VI, and indicate that the increase in the quantity of ammonium hydroxide, within the limit given, does not affect the recovery of the lead.

Estimation of Lead in Spray Residues on Apples

The samples of apples used in this work were stripped of their residue by the method of Wichmann and Vorhes (*6*).

Each apple was impaled on a pointed glass rod and swirled in a boiling sodium oleate–sodium hydroxide solution for approximately 1 minute or until the skin began to break. It was then washed with hot 1 per cent acetic acid squirted on from a short-stemmed 25-cc. pipet fitted with a rubber bulb to insure satisfactory uniform washing and keeping the volume within desired limits, and the dipping and wash solutions were combined and made up to a volume of 500 cc. with distilled water. A 100-cc. aliquot of this was added to 10 cc. of concentrated nitric acid to precipitate the soap and wax, filtered, and a suitable aliquot (1 to 5 cc.) of the filtrate was used for the determination of the lead. An aliquot should be taken so that the quantity of lead present will fall on the more sensitive portion of the curve.

Other spray residue solutions were prepared according to the method of Wichmann and Clifford (*5*). The fruit was peeled, an aliquot of the peelings was digested with nitric acid, and the acid solution was made to a volume of 500 cc. An aliquot of this was taken for the determination.

When a 1400-gram sample of apples is taken, the spray residue solution made to 500 cc., and 5 cc. of this solution are taken for the determination, the milligrams of lead read from the curve in Figure 1 are numerically equal to twice the number of grains of lead per pound of fruit.

In the authors' work the sodium oleate–hydroxide dip method, as previously described, was found most satisfactory and was adopted as routine practice. Approximately 1400 grams were taken for each sample and a 3-cc. aliquot was finally taken for the analysis. Using these quantities the lead could be determined fairly accurately as low as approximately 0.002 and as high as 0.035 grain per pound of fruit. In case the red color persisted after adding about 3 cc. of dithizone and shaking, in the procedure where the lead was extracted from the sample with the dithizone solution, the sample was discarded and a smaller aliquot was taken. The quantity of lead as read from the curve was corrected for the blank and calculated to grains per pound of fruit by the following formula:

$$\frac{\text{(Reading from curve minus blank)}}{2} \times \frac{1400}{\text{gram of fruit}} \times \frac{5}{\text{cc. of aliquot taken}} \times \frac{11}{10} = \text{grain of lead per pound of fruit}$$

For example, if a 1300-gram sample was taken, the volume of the solution was made to 500, 100 cc. of this were added to 10 cc. of concentrated nitric acid, a 3-cc. aliquot was taken, the lead found as read from the curve was 0.0200 mg. and the blank for 3 cc. was 0.0030 mg., then

$$\frac{(0.0200 - 0.0030)}{2} \times \frac{1400}{1300} \times \frac{5}{3} \times \frac{11}{10} = 0.0168 \text{ (grain per pound)}$$

Lead determinations were made on a large number of spray residues by the colorimetric method herein described and checked by the electrolytic method of Wichmann and Clifford (*5*). The close agreement of the results by the two methods is indicated by representative data in Table VII.

TABLE VII. DETERMINATIONS OF LEAD IN SPRAY RESIDUES BY ELECTROLYTIC AND COLORIMETRIC METHODS

Spray Residue Solution	Lead Found: Electrolytic	Lead Found: Colorimetric	Difference
	Gr./lb.	*Gr./lb.*	*Gr./lb.*
1038	0.0044	0.0058	+0.0014
		0.0058	+0.0014
1039	0.0045	0.0042	−0.0003
		0.0042	−0.0003
1027	0.0105	0.0103	−0.0002
		0.0103	−0.0002
1033	0.0126	0.0119	−0.0007
1025		0.0134	−0.0011
	0.0145	0.0134	−0.0011
		0.0130	−0.0015
501	0.0148	0.0136	−0.0012
1032	0.0179	0.0174	−0.0005
		0.0174	
850	0.0383	0.0370	−0.0013
		0.0380	−0.0003
1031	0.0554	0.0583	+0.0029
		0.0575	+0.0021

After some practice with the colorimetric method, an analyst can make from 30 to 36 lead determinations in 8 hours on spray residue solutions after the solutions have been prepared for analysis by either of the methods used and made to volumes of 500 cc. This includes the time necessary for the preparation of the solutions for extraction, the extractions, the colorimeter readings, and the calculations, but not the weighing and dipping of the fruit, which can be done by helpers or assistants. During the past season the procedure has been used by a control laboratory, apparently with no difficulty and with results concordant with the authors'.

Application to Animal and Plant Materials

Some work has been done on the determination of lead in biological materials. The data here reported are the results obtained on one or two samples of each kind of material and are intended simply to show the application of the method to these materials.

If the sample is a solid, place from 1 to 5 grams, depending on the amount of lead present, in a porcelain crucible and add 1 cc. of sulfuric acid (1 to 10). Add sufficient distilled water to moisten the sample completely, and mix thoroughly. Dry in an oven at 100° C. Burn in a muffle at about 500° C. If the sample is a liquid add the sulfuric acid, evaporate to dryness, and proceed as with a solid.

Moisten the ash in the crucible, add 1 cc. of concentrated hydrochloric acid, and place the crucible on a steam bath for several minutes. Add 2 cc. of nitric acid (1 to 5), transfer to a small beaker, and make just alkaline to litmus paper with ammonium hydroxide. Add 2 cc. of 5 per cent citric acid and again make

TABLE VIII. LEAD IN ANIMAL AND PLANT MATERIALS

Material	Quantity Taken	Lead Found	Material	Quantity Taken	Lead Found
	Cc.	*Mg.*		*Cc.*	*Mg.*
Blank on reagents	..	0.0040	Human urine 2	25	0.0030
		0.0046			0.0042
		0.0040			0.0038
		0.0043			0.0038
		0.0042			0.0033
		0.0038			0.0036
				Grams	
		0.0030			
		0.0040	Corn	1	0.0046
		0.0040			0.0050
		0.0036			0.0047
		0.0038			0.0044
					0.0052
Blank on reagents, plus 0.0200 mg. of lead		0.0225			
		0.0246	Wheat	1	0.0067
		0.0252			0.0056
		0.0248			0.0062
		0.0240			
				0.5	0.0030
Beef blood 1	10	0.0096			0.0032
		0.0099			
		0.0092	Alfalfa	1	0.0025
Beef blood 2	10	0.0110			0.0024
		0.0112			
		0.0108	Apple peels (oven-dried)	0.5	0.0074
		0.0108			0.0081
Human urine 1	25	0.0026	Carrots (oven-dried)	2	0.0168
		0.0027			0.0164
		0.0028			

TABLE IX. LEAD FOUND IN BONE MEAL

	Lead Added	Lead Found
	Mg.	*Mg.*
Blank	0	0.0030
		0.0027
		0.0032
Bone meal plus blank	0	0.0180
		0.0188
		0.0190
Bone meal plus blank	0.0100	0.0276
		0.0280
Bone meal plus blank	0.0200	0.0400
		0.0400

TABLE X. DETERMINATION OF LEAD IN PRESENCE OF BISMUTH AND STANNOUS TIN

Element Present	Lead Present	Lead Found
Mg.	*Mg.*	*Mg.*
Bismuth		
0.0100	0.0200	0.0196
0.0100	0.0200	0.0207
0.0100	0.0200	0.0204
0.0100	0.0200	0.0197
0.0500	0.0200	0.0196
0.0500	0.0200	0.0197
Tin		
0.0050	0.0200	0.0201
0.0100	0.0200	0.0218
0.0100	0.0200	0.0200

alkaline with ammonium hydroxide. If a precipitate forms which does not redissolve on heating, add hydrochloric acid dropwise until the solution is clear (except for a possible small amount of insoluble silicates), and 2 cc. in excess. Again make just alkaline with ammonium hydroxide. (Any precipitate that forms on making the solution alkaline occludes the lead and hence must be redissolved and held in solution. This may be accomplished by adding a large excess of sodium or ammonium chloride to the solution before neutralizing. If this does not prevent the precipitate from forming, a smaller sample of the original material should be taken for the analysis.) Add the solution to the separatory funnel containing solution E, and determine the lead as previously directed.

Table VIII gives the results of lead determinations on a few of these materials, and shows that when a lead salt was moistened with sulfuric acid and burned in a muffle at about 500° C., the lead was recovered quantitatively, and that fairly consistent results were obtained in determining lead in a few animal and plant materials.

The following statements should be made regarding the use of the method for the determination of lead in such materials as bone meal, fish meal, meat scraps, etc., which contain a very high percentage of calcium phosphate. This large amount of phosphate cannot be held in solution when the sample is made alkaline unless so small an aliquot is taken that the results are of no value. Some preliminary work was done on this kind of material and it was found that lead phosphate precipitates at a lower pH than calcium phosphate.

If ammonium hydroxide is added slowly, while stirring vigorously, to the acid solution of the above-mentioned and other similar materials until a slight permanent precipitate forms, the lead, iron, and aluminum phosphates and a small amount of calcium phosphate will be precipitated. Filter this but do not wash. Discard the filtrate and dissolve the precipitate on the filter with dilute hydrochloric acid and collect the solution in the same beaker in which the phosphates were precipitated. Wash very thoroughly with hot water. (Special care must be taken to dissolve all of the phosphate that adheres to the sides of the beaker.) Proceed as directed under plant and animal materials.

Lead was determined in 2 grams of bone meal by this method. After burning and dissolving the meal, the solution was made to a volume of 200 cc. and 10-cc. aliquots were taken (0.1 gram) for analyses. The results are shown in Table IX and indicate that added lead can be recovered quantitatively by the above method and that duplicate and triplicate results are in close agreement; hence the method should be applicable to materials high in calcium phosphate.

Interfering Elements

Bismuth, stannous tin, and thallium combine with dithizone dissolved in chloroform and like lead form intensely colored solutions. Bismuth forms a brown color, stannous tin a red color of a different tint than that of lead, and thallium a cherry-red color which cannot be distinguished from lead. If any of these elements are present with the lead in the ammoniacal citrate-cyanide solution from which the lead is to be extracted they will be extracted with the lead. Fortunately, however, the bismuth and stannous tin dithizone compounds are soluble in solutions E and F containing an excess of ammonium hydroxide. Hence, if 10 cc. of concentrated ammonium hydroxide are added to each 500 cc. of solutions E and F and the samples are treated in the usual manner, the bismuth and stannous tin are removed while the lead remains. When there is a large amount of bismuth present it is usually necessary to make an extra extraction with solution F. Table X shows that, with the above changes in the procedure, lead may be determined accurately in the presence of these elements.

Unfortunately thallium is not soluble in solution F and hence when present interferes with the determination of lead.

An attempt was made to use carbon tetrachloride instead of chloroform as a solvent for the dithizone for extracting the lead. Lead combines with dithizone when dissolved in carbon tetrachloride as well as when dissolved in chloroform, and the excess of dithizone is removed more easily by the ammoniacal solution from the carbon tetrachloride layer than from the chloroform layer. However, the lead dithizone compound is slowly extracted from the carbon tetrachloride layer by the ammoniacal solution and furthermore is not so stable as in chloroform solution, and therefore carbon tetrachloride cannot be used for accurate quantitative determinations.

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Oxidation-Reduction Indicators

I. Diphenylbenzidine Sulfonic Acid

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IT HAS already been pointed out (*2*) that diphenylbenzidine disulfonic acid is an intermediate product in the oxidation of diphenylamine sulfonic acid to its violet colored holoquinoid form, and that it should possess all the advantages of the latter indicator, yet require a much smaller correction when used with dilute oxidizing solutions.

The authors, accordingly, have tried a number of possible means of synthesis; but only the direct sulfonation of diphenylbenzidine gave any promise of success. This reaction proceeds vigorously, and one or more of the poly-sulfonic acids may be easily obtained.

Preparation of Sodium Diphenylbenzidine Sulfonate

One gram of dry powdered diphenylbenzidine, prepared as described in a recent paper (*1*), is added little by little to 10 ml. of 60 per cent fuming sulfuric acid in a shallow dish over a period of about 2 minutes. The mixture heats up, but should not be allowed to become warmer than 40° C. As complete solution as possible is obtained by stirring and mashing up any lumps with a rod; then, after not more than 3 minutes, it is poured onto ice. Difficulty in controlling the reaction makes it undesirable to work with larger quantities, but the products of as many portions as desired may be combined at this point, and diluted to a volume of 200 ml. for each gram of diphenylbenzidine used.

The solution is then heated to boiling, and the green color reduced to brown with a stream of sulfur dioxide; the excess of the latter is removed by boiling, and any charred material filtered off. The filtrate is carefully neutralized with sodium carbonate, diluting if any precipitation occurs, and the sodium sulfate rendered insoluble by the addition of four volumes of ethyl alcohol; the sodium diphenylbenzidine sulfonate is appreciably soluble in 80 per cent alcohol, while all but an extremely small amount of the sodium sulfate is precipitated. After filtering, the residue should be redissolved in water, and reprecipitated with alcohol as often as necessary to secure complete removal of the yellow color; the total volume of the combined filtrates is usually about 5 liters for each gram of diphenylbenzidine used. The alcohol is boiled off rapidly, and the evaporation completed on a steam bath, avoiding long exposure or overheating of the residue, which should be a light yellow. The yield is 3 to 4 grams per gram of diphenylbenzidine used.

Composition of Sulfonated Product

Microscopic examination showed no appreciable quantity of sodium sulfate to be present; moreover, the known insolubility of this salt in 80 per cent alcohol precludes such a possibility. Chemical analysis indicated that ten sulfonate groups had been added in most cases; products prepared with 25 per cent fuming sulfuric acid contained four sulfonate groups. Exact information as to the positions of the substituted groups in the molecule would be difficult to obtain, and is not necessary for the present purpose. Presumably, several different poly-sulfonic acids might be produced under different experimental conditions.

STOCK SOLUTION OF INDICATOR. A 0.1 per cent solution of the sodium diphenylbenzidine sulfonate in water is recommended; this can be kept for several months, but not indefinitely. One drop or even less of this solution is satisfactory for titrations with 0.01 or 0.001 *N* solutions; 10 drops are preferable when 0.1 *N* solutions are used.

Indicator Properties

As might be expected, diphenylbenzidine sulfonic acid strongly resembles diphenylamine sulfonic acid in most of its properties. When small amounts are oxidized in 0.5 to 1.0 *N* sulfuric acid solution, the pale yellow becomes first deep yellow, then green, and finally violet. Upon reduction, the color changes are reversed. It works perfectly in the presence of tungstate, and its color development is extremely sensitive to the catalytic effect of traces of ferrous iron, when dichromate is used as the oxidant. In such a case, back-titration with ferrous solution, after treatment with an excess of oxidant, is more reliable; the error involved by even 10 minutes' contact with a reasonable excess of dichromate is negligible. For accurate microanalysis, the indicator corrections should be determined experimentally, but they are approximately equal to the volumes of indicator used, in terms of a 0.001 *N* solution.

ABSORPTION SPECTRA. When diphenylbenzidine sulfonic acid is fully oxidized by dichromate, permanganate, or ceric sulfate, reddish violets are produced which are stable, but which fade after a long time. Bromine yields blues which fade very rapidly. The half-oxidized green form, on the other hand, is extremely stable, and does not precipitate out on standing, as was the case with that resulting from diphenylamine or diphenylbenzidine. Absorption curves were determined with a Keuffel and Esser color analyzer, the violet form giving one similar to that for diphenylamine sulfonic acid violet (*2*), with a maximum at 5600 Å., while the green has a minimum at this point, and absorbs strongly at both ends of the visible spectrum.

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Determination of Small Amounts of Potassium by Means of Sodium Cobaltinitrite

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Experimental investigation of the precipitation of potassium as sodium-potassium cobaltinitrite indicates that the precipitate obtained varies in composition with respect to potassium content, depending upon the conditions of precipitation. The composition of the precipitate varies but lies between $KNa_2[Co(NO_2)_6]$ and $K_2Na[Co(NO_2)_6]$.

IN THE COURSE of a study of the colorimetric estimation of small amounts of potassium by precipitation as potassium sodium cobaltinitrite it was necessary to establish the relationship between the concentration of potassium and the composition of the precipitate obtained with sodium cobaltinitrite under various conditions. Accordingly solutions containing various amounts of potassium sulfate were analyzed by Taylor's (*11*) procedure and by precipitation with sodium cobaltinitrite prepared according to Biilmann (*2*), the potassium being precipitated in a water-alcohol solution saturated with sodium chloride. In a third series of experiments potassium was precipitated from water-alcohol potassium chloride solutions with Biilmann's preparation, but the precipitate was settled with the aid of a centrifuge and a different method of washing was used.

Precipitation by Taylor's Procedure

The procedure described by Taylor (*11*) was used to precipitate potassium from a series of standard potassium sulfate solutions of known concentration ranging from 0.20 to 1.00 mg. of potassium per cc. The results obtained in this series of determinations are compared with the results obtained by alternate procedures in Table I.

TABLE I. COMPOSITION OF COBALTINITRITE PRECIPITATE

Potassium in Sample	Wt. of Precipitate	Potassium in Precipitate (Calcd.)	Cobalt in Precipitate
Mg.	*Mg.*	%	%
	Taylor's Procedure		
0.20[a]	1.601	12.5[b]	...
0.49	3.991	12.3	...
0.70	5.276	13.3[c]	...
1.00	7.689	13.0	...
	Precipitation in Water-Alcohol Solution Saturated with NaCl		
0.10[a]	0.612	16.4	...
0.50	3.672	13.4	...
1.00	7.937	12.6[d]	...
	Precipitation in Water-Alcohol Solution with Centrifuging		
0.489[e]	3.65	13.40[d]	12.85
1.953	14.2	13.77	13.09
4.899	34.15	14.32	13.51

[a] As K_2SO_4.
[b] In calculating the percentage of potassium in the precipitates it was assumed that all the potassium taken was precipitated.
[c] The cobalt reagent in this case was 10 days old. For all other precipitations in these experiments freshly prepared cobalt reagent was used. The cobalt reagent undergoes continuous decomposition even when tightly stoppered and in an ice box.
[d] 1.00 mg. of potassium precipitated according to the same procedure, with the exception of time held in the ice box which was 11 instead of 24 hours, gave a precipitate in which the calculated potassium content was 12.3 per cent.
[e] As KCl.

Precipitation in Water-Alcohol Solution Saturated with Sodium Chloride

Table I also presents the results obtained when a series of potassium sulfate solutions of known concentration were precipitated in a water-alcohol solution saturated with sodium chloride, using a purified sodium cobaltinitrite prepared according to Biilmann (*2*). Earlier investigators using Biilmann's sodium cobaltinitrite for quantitative determination of potassium include Gram (*5*)[1] and Tischer (*12*). Christensen and Feilberg (*4*), Jander and Faber (*7*), and Bonneau (*3*) have studied the precipitation of potassium in the presence of sodium chloride also.

In the course of these experiments the author found that the cost of preparing the sodium cobaltinitrite could be reduced by using dry acetone, instead of the absolute alcohol and absolute ether of the original method, for drying the precipitate of sodium cobaltinitrite. He also found it advisable to keep the dried sodium cobaltinitrite tightly stoppered and in a cool dark place, which precautions permitted him to keep the material for more than 6 months without decomposition. A further precaution recommended in the use of this preparation for precipitation of potassium is to dissolve it freshly, to be used immediately for the precipitation.

The procedure used for precipitation in this second series was essentially the same as that (*11*) used in the first series, except for a different cobaltinitrite reagent and a slightly different method of washing the precipitate.

Precipitation in Water-Alcohol Solution with Centrifuging

The third series presented in Table I involved a precipitation and washing procedure developed by the author on the basis of extensive experience in estimating small amounts of potassium in extracts from potash-bearing minerals and from soils.

Five cubic centimeters of a potassium chloride solution were mixed thoroughly with 1.25 cc. of 96 per cent alcohol in a graduated conical centrifuge tube, 5 cc. of a 20 per cent solution of Biilmann's sodium cobaltinitrite were added, and the solutions were thoroughly mixed by shaking. The tubes were stoppered, held in an ice box for 24 hours at 2° to 3° C., and then centrifuged and the supernatant liquor was carefully removed. The precipitate was washed three times with 10 cc. of 48 per cent alcohol, suspending the precipitate after the second washing and, finally, was washed with absolute alcohol and dry acetone. The last traces of acetone were removed in a vacuum desiccator. After weighing the precipitate, the cobalt was converted into the sulfate and the cobalt content estimated electrolytically according to Pregl's (*9*) procedure.

Discussion

The experiments performed indicate that reasonably consistent results may be obtained by using recrystallized sodium cobaltinitrite as the reagent for precipitating potassium. It is evident, however, that the potassium content of the precipitate depends upon the concentration of potassium in the solution analyzed and upon the procedure followed in making the precipitation. The results of the present experiments are in agreement with observations made by Tischer (*12*), Gram (*5*), and Benedetti-Pichler (*1*).

The chemical composition of the precipitate, on the basis

[1] The author's study had been completed when he first learned of Gram's (*5*) investigation.

of the calculated potassium content, is between $KNa_2[Co(NO_2)_6]$, which contains 9.3 per cent of potassium, and $K_2Na[Co(NO_2)_6]$, which contains 17.9 per cent of potassium. Studies by Jander and Faber (*7*), Lewis and Marmoy (*8*), and Sobel and Kramer (*10*) also indicate this. Since the potassium and sodium content of the precipitate varies with the conditions of precipitation, the formula $(K/Na)_3[Co(NO_2)_6]$, with K/Na denoting the variable composition, has been suggested to designate this precipitate. Hamburger (*6*) has proposed a similar formula.

Conclusions

In the quantitative determination of potassium by precipitation with sodium cobaltinitrite it is necessary to take into account the fact that the potassium content of the precipitate is a function of the method of precipitation and the potassium concentration in the solution being analyzed. There seems to be a need for a very thorough analytical investigation in order to develop a satisfactory standard method for estimating small amounts of potassium by precipitating the potassium as sodium–potassium cobaltinitrite.

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Determination of Molybdenum in Plants and Soils

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IN STUDIES made by the Department of Research Chemistry, University of Wyoming, on toxic minerals in native vegetation occurring on Cretaceous and post-Cretaceous shales, it has been observed that molybdenum is strongly indicated in some instances as being a contributing factor in the poisoning of range livestock. By growing barley on experimental plots that were treated with sodium molybdate, it has been possible to determine, by the exclusion of selenium, the pathological conditions resulting from feeding livestock upon such grain. Chronic poisoning has been produced experimentally and the symptoms exhibited are like those produced by selenium in cereals.

A survey of the methods in the literature for the determination of molybdenum showed the necessity of adapting them to plant and soil analysis. Most of these methods were concerned with the analysis of less complex mixtures containing relatively large amounts of molybdenum. In the analysis of plants and soils there is seldom more than a fraction of a milligram of the element present in 100 grams of sample. Owing to the presence of large amounts of the common elements, as well as smaller amounts of the rarer elements having similar properties to those of molybdenum it was necessary that the method developed be specific for this element.

Determination of Molybdenum in Plants

Approximately 100 grams of the air-dried sample were moistened with concentrated sulfuric acid, warmed to remove the excess acid, and slowly ignited, with occasional stirring, in an electric muffle furnace at a temperature preferably below 500° to 550° C. (*4*). The ash was then extracted with dilute hydrochloric acid, filtered, and the remaining residue, which contained some carbon, again ignited. The remaining ash was extracted with dilute hydrochloric acid, filtered, and the residue warmed for 1 hour upon a steam bath with a mixture of hydrochloric and nitric acids. After diluting with water, the mixture was filtered, washed thoroughly with water, and the colorless siliceous residue discarded. The filtrate and washings from the latter treatment were then evaporated to dryness to remove the nitric acid, the residue was taken up in dilute hydrochloric acid, and the acid solution united with the hydrochloric acid extracts previously obtained.

In case tungsten was thought to be present (*6*), 5 grams of tartaric acid were added, and the solution was made strongly alkaline with ammonia and saturated while cold with hydrogen sulfide. The brown molybdenum trisulfide, MoS_3, was precipitated by cautiously pouring the alkaline solution into an excess of 6 *N* sulfuric acid (or 6 *N* hydrochloric acid if considerable calcium was present) and heated to boiling to coagulate the precipitate. In case the presence of vanadium was suspected, the molybdenum was precipitated free of vanadium by saturating the slightly acid solution with hydrogen sulfide and heating 30 minutes in a pressure bottle placed in boiling water.

After filtering off the molybdenum sulfide, it was washed with a cold saturated solution of hydrogen sulfide and redissolved by pouring repeatedly through the filter a warm solution of one part of 6 *N* hydrochloric acid and one part of concentrated nitric acid. The filtrate and washings were evaporated to dryness, and the residue was taken up in a drop or two of concentrated nitric acid, evaporated just to dryness (to oxidize the molybdenum to the hexavalent state), and finally taken up in water and 0.5 ml. of 6 *N* hydrochloric acid, or a sufficient amount to make the aliquot used contain 0.5 ml. of the acid.

To confirm the presence of molybdenum, an aliquot of the solution was treated with either of the following reagents:

1. A few crystals of potassium ethyl xanthate stirred with the slightly acid solution containing 0.001 mg., or more, of molybdenum gave a distinctive rose coloration (*7*, *10*).
2. A drop of a suitable reducing agent, such as stannous chloride or sodium thiosulfate solution, was stirred with the unknown to reduce any ferric iron present (which would interfere with the test) and to reduce the hexavalent molybdenum. The addition of a drop of sodium or potassium thiocyanate solution gave a red coloration that was easily detected in the presence of 0.001 mg. of molybdenum (*1*, *3*, *11*).

In case the molybdenum sulfide precipitate indicated the presence of 5 mg., or more, of molybdenum it was determined gravimetrically as lead molybdate.

The unknown solution, or aliquot, was made alkaline with ammonia, heated to boiling to precipitate any impurities of iron and aluminum, filtered, and the filtrate made just acid with hydrochloric acid. After the addition of 5 ml. of glacial acetic

acid and 25 ml. of 25 per cent ammonium acetate, the solution was heated to boiling and the lead molybdate precipitated by the dropwise addition of 5 ml. of 4 per cent lead acetate solution. A large excess of lead acetate should be avoided, owing to the possible formation of lead sulfate to give accordingly high results (*2, 5, 9*). The solution was allowed to stand upon a hot plate just below boiling for 30 minutes to permit the precipitate to coagulate, then set aside overnight for the precipitate to settle. After filtering through a Gooch crucible, the lead molybdate was washed with hot water, or with a 2 to 3 per cent ammonium acetate solution if the amount of the precipitate was large, ignited at a dull red heat, then cooled and weighed. The weight of molybdenum present in the aliquot was equivalent to the weight of the lead molybdate found multiplied by the chemical factor 0.2614.

Table I gives the results obtained in the analysis of two samples for molybdenum.

TABLE I. DETERMINATION OF MOLYBDENUM

Sample	Plant	Weight of $PbMoO_4$	Molybdenum
		Gram	*P. p. m.*
A295	Barley hay	0.0086	90
	Barley hay, check	0.0084	88
A237	Alfalfa	0.0014	7
	Alfalfa, check	0.0013	7

To determine the molybdenum content of most plants, which generally contained less than 5 mg. of molybdenum per 100 grams of sample, it was more convenient and accurate to use a colorimetric method.

An aliquot of the unknown solution containing 0.5 ml. of 6 *N* hydrochloric acid was treated with 1 ml. of 1 *N* potassium thiocyanate and 2 ml. of 1 *N* stannous chloride solution, and immediately extracted with butyl acetate (*8*). A sufficient amount of this solvent should have been previously shaken with the stannous chloride and potassium thiocyanate solutions and separated from the aqueous layer before being used in the extraction. As the color is increasingly unstable in an aqueous solution in proportion to the amount of acid present, equal amounts (or 0.5 ml. of 6 *N* hydrochloric acid) were used in both the standard and unknown solutions. Approximately one-half of the total butyl acetate was used in the first extraction, followed by three or more extractions with smaller amounts until these were entirely colorless. The total volume of extract may vary from approximately 5 ml. for 0.001 mg. of molybdenum to about 25 ml. for 10 mg. of molybdenum. Any turbidity due to water may be removed by the addition of a few drops of alcohol.

A standard color was prepared by treating a suitable volume of a known solution of molybdenum as ammonium molybdate in the same manner as the unknown. To obtain the most accurate result, the concentration of the molybdenum in the standard and the unknown should be nearly equal. The ammonium molybdate solution was prepared by dissolving 2.0425 grams of the salt in water and making it to one liter. One milliliter of this solution contained 1 mg. of molybdenum. Other standard solutions containing 0.1, 0.01, or 0.001 mg. of molybdenum per milliliter were prepared by the dilution of this solution.

The colored extracts of the unknown and standard solutions were made to the same volume with butyl acetate and their relative concentrations determined by the comparison of their color intensities in a Bausch and Lomb colorimeter. By the substitution of these average values in the following equation the number of milligrams of molybdenum in the aliquot were calculated:

$$\text{Mg. of Mo in unknown} = \frac{\text{mg. of Mo in standard} \times \text{av. reading of standard}}{\text{av. reading of unknown}}$$

To determine the accuracy of the colorimetric method, known solutions of molybdenum were tested and gave the results shown in Table II.

TABLE II. COLORIMETRIC DETERMINATION OF MOLYBDENUM

Extracts	Mo Used	Av. Reading	Mo Used	Av. Reading	Mo Calculated	Error	
Ml.	*Mg.*		*Mg.*		*Mg.*	*Mg.*	*%*
7	0.001	15	0.001	15.05	0.00096	0.00004	4
10	0.01	30	0.01	30.16	0.0095	0.0005	5
10	0.07	20	0.05	27.50	0.051	0.001	2
15	1.00	40	0.90	44.99	0.89	0.01	1
25	10.00	70	10.00	69.90	10.02	0.02	0.2

The average error in the analysis of thirty-three known solutions containing from 0.001 to 10.00 mg. of molybdenum was 4.6 per cent. Hence, the accuracy with which the molybdenum in the molybdenum sulfide precipitate was determined was approximately 95 per cent.

Determination of Molybdenum in Soils

Molybdenum was determined in soils in much the same manner as described above for its determination in plants, except that a larger amount of material was used.

Approximately 200 grams of the soil were covered with dilute hydrochloric acid, warmed upon a steam bath for 24 hours, filtered, and washed. The residue was repeatedly treated in the same manner with a mixture of hydrochloric acid and nitric acid until only a colorless residue remained. After the removal of the nitric acid by evaporation, the extracts were combined and the molybdenum sulfide was precipitated as described. Because of the large amount of material dissolved by the acid solutions, it was generally necessary to reprecipitate the molybdenum sulfide from the hydrogen sulfide precipitate before attempting its estimation. The minimum amount of molybdenum present as molybdenum sulfide that it was possible to determine by this colorimetric method was 0.001 mg.

The results shown in Table III were obtained in the analysis of several soil samples for molybdenum.

TABLE III. DETERMINATION OF MOLYBDENUM IN SOILS

Sample	Type of Soil	Molybdenum
		P. p. m.
A779	Iron concretions from Niobrara	20
A785	Iron concretions from Niobrara	15
A777	Shell layer from Niobrara	5
A103	Alkali seep	5
A150	Niobrara shale	1.0
A104	Alkali layer from Niobrara seep	0.8
A137	Niobrara shale	0.5
A169	Niobrara wash	0.08

Summary

A gravimetric method is described for the determination of molybdenum as lead molybdate in plants and soils in amounts exceeding 5 mg. A colorimetric method based upon the extraction of the red colored molybdenum thiocyanate by butyl acetate is described for the determination of molybdenum in plants and soils.

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A Procedure for Classification of Hydrocarbons

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A method for use in qualitative organic analysis is described, whereby a hydrocarbon may be experimentally classified according to its structure. The procedure is based upon miscibility of the hydrocarbon with nitromethane, aniline, and benzyl alcohol, upon the bromide-bromate titration of unsaturation, and upon the usual constants—melting point, boiling point, and density.

BECAUSE of the frequent similarity in reactions and constants of hydrocarbons possessing different structures, the usual procedures for qualitative identification of organic compounds have not, in the past, included many details concerning this class of compounds which is rapidly growing in both scientific and commercial importance. The method described in this paper was developed to replace that used for Genus IX (hydrocarbons) by Mulliken (*3*). The system now used divides the liquid hydrocarbons into three groups, depending upon their density and their reactivity with bromine, nitric acid, and sulfuric acid. By means of density, the aromatics and other heavy hydrocarbons are classified apart from the acyclics and lighter cyclics, which are divided into two groups upon the basis of their behavior with the reagents named.

By means of the procedure described in this article, the genus is subdivided into a larger number of sections, making it possible to classify a hydrocarbon of unknown structure, experimentally and quickly, according to the following scheme:

A. Gaseous hydrocarbons
B. Liquid hydrocarbons
   1. Aromatics, etc.
   2. Unsaturated nonaromatics, other than alkenes
   3. Alkenes
   4. Cycloalkanes
   5. Alkanes
C. Solid hydrocarbons
   1. Aromatics
   2. Nonaromatics

The method combines miscibility with various selective solvents, bromide-bromate titration, density, and boiling point (and melting point for solids).

Gases

So few gaseous hydrocarbons exist (22 in all, *2*) that they may be grouped together without further subdivision.

Liquids

All aromatic hydrocarbons have a density greater than 0.84 at 20°/4°. Hence, if the density of an unknown hydrocarbon is less than that, it cannot be aromatic. It does not follow, however, that if its density is greater it is aromatic.

It has been found by the authors that nitromethane may be used to distinguish between most aromatic and nonaromatic hydrocarbons, the former being miscible, the latter immiscible at a given temperature, depending upon the molecular weight or boiling point of the hydrocarbon.

The data may be summarized by Figure 1 in which the dots represent the solubility temperatures of equal volumes (0.1 cc.) of aromatic hydrocarbon and nitromethane—i. e., the temperature at which cloudiness first appears in a homogeneous solution on cooling—and the circles represent similar temperatures for nonaromatics, exclusive of acetylenes and a few allenes and conjugated diolefins. All the dots fall within the shaded area below. All the circles fall within the shaded area above. Hence, by determining the miscibility with nitromethane at a temperature included within the intermediate clear zone, preferably along the line *AB*, an unknown hydrocarbon can be classed as aromatic or nonaromatic, unless it be an acetylene, allene, or conjugated diolefin.

Sixty hydrocarbons, in addition to those shown by Figure 1, have been found miscible if aromatic, or immiscible if nonaromatic, at the temperatures indicated by *AB* (*7*). This additional list includes the following aromatics: benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene, phenylacetylene, styrene, propylbenzene, mesitylene, *tert*-butylbenzene, pseudocumene, hydrindene, 1-phenyl-1-pentene, dihydronaphthalene, 4-benzylideneheptane, α- and β-methylnaphthalene, diphenylmethane, 1,6-dimethylnaphthalene, and 1,1-diphenyl-1-propene. Of aromatics having a single side chain, the highest tested were: with saturated chain, *tert*-amylbenzene and phenylcyclohexane; with unsaturated chain, 2-phenyl-3-isopropyl-4-methyl-2-pentene.

The extent to which this procedure can be relied upon for other compounds of this type has not been determined. It should be used with caution when possibly in their presence.

Nonaromatics of the same degree of unsaturation as aromatics have not been dealt with experimentally, save in the case of the sesquiterpenes caryophyllene and cedrene. These two compounds are properly classified among the nonaromatics. It is possible that some of these compounds, such as the fulvenes, might be classed with the aromatics by this procedure.

The test is carried out by measuring 0.10 cc. of hydrocarbon (0.08 gram, if solid) and an equal volume of solvent into a glass-stoppered tube of 4 mm. inside diameter. The tube is strapped to a thermometer, shaken, and warmed a few degrees above the temperature of observation. It is then cooled slowly, with shaking, in an appropriate bath, and the number of phases noted at the desired temperature.

If the compound is an acetylene, allene, or conjugated diolefin, it may possess a solubility such as to make it fall among the aromatics, but its density will be less than 0.84 at 20°/4°. Occasionally one may have to deal with a cycloalkine, such as cyclohexyl acetylene, and be led to classify it among the aromatics upon the basis of its miscibility with nitromethane and its density. For such compounds now known, the latter lies between 0.84 and 0.86 at 20°/4°. Although cycloalkines have not been tested in this investigation, a number of alkines (1-heptine, 2-heptine, 3-heptine, 1-octine, 2-octine, 4-nonine, and 1-hexadecine) were found to be completely miscible with an equal volume (0.1 cc.) of sulfuric acid (d. 1.84) at 20°, with production of a red color, giving rise to a water-immiscible oil of pleasant, ketone-like odor

[1] Professor Mulliken passed away at his home in Newburyport, Mass., on October 24, 1934, deeply regretted by the members of his profession and by his many other friends.

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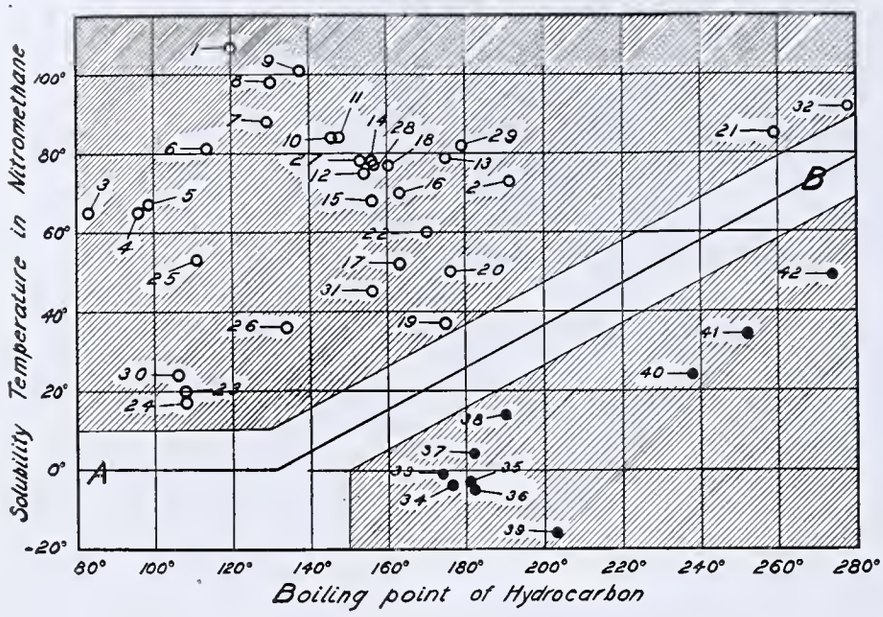

FIGURE 1. SOLUBILITY OF HYDROCARBONS IN NITROMETHANE
TEMPERATURES IN ° C. ○ NONAROMATIC. ● AROMATIC

1. Dimethylcyclohexane
2. *tert*-Amylcyclohexane
3. 2,4-Dimethyl-2-pentene
4. 3-Heptene
5. 2-Heptene
6. 4-Methyl-2-heptene
7. 4,5,5-Trimethyl-2-hexene
8. 4,6-Dimethyl-2-heptene
9. 4-Methyl-2-octene
10. 1-Nonene
11. 4-Nonene
12. 1-Cyclohexyl-2-propene
13. *d*-Menthene
14. *d*-α-Pinene
15. *l*-α-Pinene
16. *l*-β-Pinene
17. Sabinene
18. Camphene
19. Phellandrene
20. *d*-Limonene
21. Caryophyllene
22. Dicyclopentadiene
23. 2,2-Dimethyl-3,4-hexadiene
24. 2,4-Heptadiene
25. 4-Methyl-1,5-heptadiene
26. 2,4-Octadiene
27. 4,5-Dimethyl-2,6-octadiene
28. 4-Propyl-1,5-heptadiene
29. 4-Allyl-2-octene
30. 3-Heptine
31. 4-Nonine
32. 1-Hexadecine
33. *sec*-Butylbenzene
34. *p*-Cymene
35. *m*-Diethylbenzene
36. *p*-Diethylbenzene
37. *n*-Butylbenzene
38. *tert*-Amylbenzene
39. Tetrahydronaphthalene
40. Phenylcyclohexane
41. 2,4-Dimethyl-3-benzylidenepentane
42. 2-Phenyl-3-isopropyl-4-methyl-2-pentene

Boiling points at atmospheric pressure for 32, 41, and 42 are estimated.

upon aqueous dilution. The aromatics of density less than 0.86 at 20°/4° have saturated side chains and are not completely miscible with sulfuric acid at 20°, although they may be partially attacked. Hence, if the density of the compound lies within these limits, it is well to add this test, which should be carried out by cooling the acid and hydrocarbon to 0° before mixing and allowing them to warm to room temperature afterwards, if necessary.

By combining these three tests, an aromatic hydrocarbon may, in general, be distinguished from a nonaromatic.

If the unknown hydrocarbon is nonaromatic, the bromide-bromate titration will show the presence or absence of unsaturation, and will give an approximate value of the number of double bonds present, save in the case of alkines and certain unsaturated cyclic compounds (*6*). If it is unsaturated and reacts with more than three atoms of bromine per molecule, then it is some type other than alkene. If it reacts with less than this amount of bromine, it may or may not be an alkene.

The number of atoms of bromine used up in this titration may be readily calculated, given the molecular weight of the hydrocarbon. This may be determined experimentally, but usually it may be estimated from the boiling point with a degree of approximation sufficient for this calculation. If 0.5 cc. of hydrocarbon is titrated and VNM/G is greater than 1500, then the hydrocarbon has reacted with more than three atoms of bromine per molecule. V is the volume of bromide-bromate solution used up, N is its normality, M is the molecular weight of the unknown, and G its density.

If the hydrocarbon reacts with less than three atoms of bromine, its nature can be determined more precisely by testing its miscibility with aniline at the temperature indicated by Table I, whose figures correspond to a stepwise equivalent of a line constructed from experimental data in a manner similar to *AB* of Figure 1. The alkenes are immiscible with aniline at the temperatures given, whereas acetylenes (as well as allenes, conjugated diolefins, etc.), which might perhaps not react with more than three atoms of bromine, are miscible (*7*).

Twenty-three olefins of several types, C_6 to C_{16}, were found immiscible at the temperatures of Table I, whereas eight acetylenes, C_5 to C_{16}, were found miscible.

While cyclic unsaturated hydrocarbons will often be miscible with aniline at these temperatures, certain of the less common ones may not be. Density offers a means of distinguishing the latter from alkenes. The acyclic olefins thus far described in the literature have densities below the figures of Table II, the cyclics above (save for a few rare exceptions, probably provided for by the aniline miscibility test).

By combining these tests, it is possible to differentiate saturated from unsaturated nonaromatic hydrocarbons, and to distinguish acyclic olefins among the latter.

It remains to determine whether an unknown, if saturated, is of open or closed chain. For this purpose one may use either the density of the hydrocarbon or its miscibility with benzyl alcohol (*1*). If the latter method is chosen, miscibility may be tested at the temperatures indicated by Table III. If the compound is miscible with benzyl alcohol at the temperature specified, it is cyclic; otherwise it is acyclic. (Eight paraffins, C_6 to C_{14}, and eight cycloparaffins, C_6 to C_{11}, were tested, *7*.)

The entire procedure for liquid hydrocarbons may be summarized by Figure 2. The section for hydrocarbons of boiling point 20° to 70° is constructed like the part already described,

TABLE I. TEMPERATURES FOR DETERMINATION OF MISCIBILITY OF HYDROCARBONS WITH ANILINE

Boiling Point of Hydrocarbon ° C.	Determination of Miscibility with Aniline ° C.
70–130	0
130–190	15
190–240	30
240–285	45

TABLE II. DENSITY LIMITS OF OLEFINS

Boiling Point ° C.	Density Limit at 20°/4°
20– 40	0.70
40– 70	0.73
70–100	0.75
100–130	0.77
130–190	0.79
190–230	0.81
230–300	0.83

TABLE III. TEMPERATURES FOR DETERMINATION OF MISCIBILITY WITH BENZYL ALCOHOL

(For alkanes and cycloalkanes)

Boiling Point of Hydrocarbon ° C.	Determination of Miscibility with Benzoyl Alcohol ° C.
20– 70	20
70–130	30
130–190	50
190–250	70

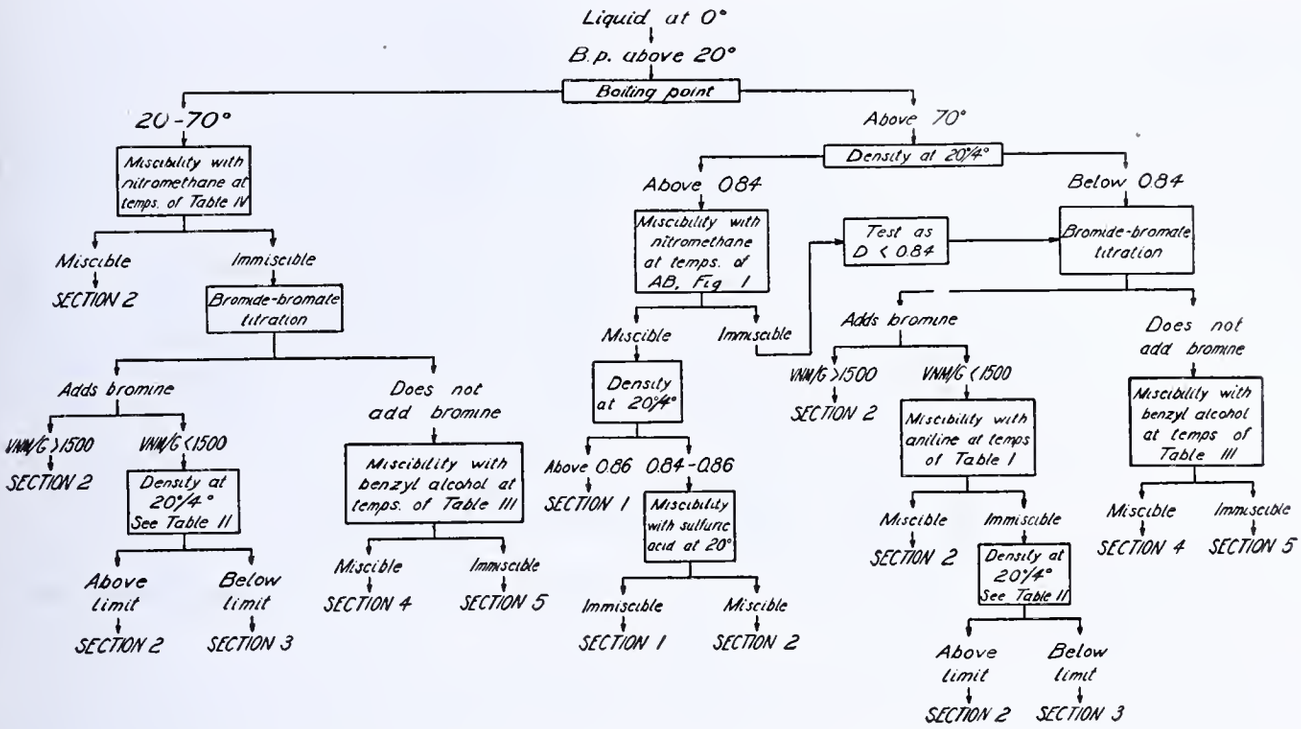

FIGURE 2. CHART FOR EXPERIMENTAL CLASSIFICATION OF LIQUID HYDROCARBONS

Section 1. Aromatics, etc.
Section 2. Alkadienes, alkines, cycloalkenes, terpenes, etc.
Section 3. Alkenes
Section 4. Saturated cyclics
Section 5. Alkanes

miscibility with nitromethane at the temperatures of Table IV being the first criterion for subdivision. Those hydrocarbons which are more highly unsaturated than the alkenes are miscible at the temperatures given; others are immiscible.

Solids

If the hydrocarbon is solid at 0° C., the matter is more simple, as the majority of such compounds are aromatic. There are, indeed, so few nonaromatics of melting point above 120° that it is not worth while to develop a general procedure capable of distinguishing them from the others. Because of the small number of nonaromatics among them, solid hydrocarbons have not been examined by the authors in as great detail as the liquids. It appears, however, that, with a few exceptions, among those melting below 120° aromatics can be distinguished from nonaromatics as indicated by Table V. If the hydrocarbon (0.08 gram) is soluble in nitromethane (0.1 cc.) at the temperature given in the third column, it is aromatic; otherwise it is nonaromatic. (About thirty-five compounds have been examined, no exceptions to Table V having been found among them.)

The procedure described makes it possible to list the hydrocarbons in divisions of solids, liquids, and gases, each of which is subdivided into sections, according to the classical method of Mulliken's works. (A catalog of the nonaromatics known up to 1928 and the aromatics to 1910 has been prepared in this form. The hydrocarbons are listed in the order of their melting or boiling points. Densities and refractive indices are tabulated, together with methods of specific characterization, where possible, *9*.) Although it may appear somewhat complicated for a qualitative scheme, it is simple in technic. Any hydrocarbon can be properly classified in a half hour, or less, and only a few tenths of 1 cc. of compound are consumed in the tests. It has the advantage of leaving little ambiguity as to the nature of an unknown hydrocarbon, although the customary limitations, as well as justifications, of organic qualitative analysis apply (*5*). It has been developed by considering the best data given in the literature for about 2000 hydrocarbons and the results of experimental work with about 200 different ones, including representatives of all the most important types of each of the sections. A complete list of the compounds tested is too long to include here. The procedure, practically as outlined, has been used successfully during the past several years in courses in organic qualitative analysis at the Massachusetts Institute of Technology. According to the empirical tests described by Mulliken (*3*), many ethers would be classified as hydrocarbons. According to the procedure of this paper, some of these will be classified as aromatics, others as nonaromatics. Many of the latter may be easily distinguished from hydrocarbons by their behavior with concentrated sulfuric acid (*4*) or concentrated hydrochloric or hydrobromic acid (*8*).

TABLE IV. TEMPERATURES FOR DETERMINATION OF MISCIBILITY WITH NITROMETHANE

(For hydrocarbons of b. p. 20° to 70°)

Boiling Point of Hydrocarbon ° C.	Determination of Miscibility with Nitromethane ° C.
20–40	0
40–70	15

TABLE V. TEMPERATURE FOR DETERMINING SOLUBILITY IN NITROMETHANE

Boiling Point of Hydrocarbon ° C.	Melting Point of Hydrocarbon ° C.	Determination of Solubility in Nitromethane ° C.
Below 190	0–120	25
Above 190	0– 40	65
	40–120	100

Acknowledgment

Samples were obtained of all hydrocarbons available from Eastman, Kahlbaum, and the British Drug Houses. A considerable number of others were synthesized with the aid of H. T. Gerry and with financial assistance from a grant to S. P. Mulliken from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences, for which the authors wish to express their appreciation. Valuable contributions were also received from several chemists, whose kindness is hereby

acknowledged; several samples of highly purified olefins and paraffins from H. C. Buc of the Standard Oil Development Co.; a number of aromatics containing unsaturated side chains (up to C_9 side chain) from President Conant of Harvard University; several aliphatic diolefins from Frank Cortese; and a number of valuable terpenes, sesquiterpenes, and related compounds from Schimmel & Co., through the courtesy of F. E. Watermeyer, president of Fritzsche Bros., their American representatives.

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The Evap-O-Rotor

A Device for Comparing the Evaporation Rates of Lacquer Solvents

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Among the tests employed in the lacquer industry to control and judge the performance of the product, the determination of rates of evaporation of the volatile solvents holds an important place. This test, if carried out on a comparative basis, furnishes a measure of the relative drying times of lacquers, and as a consequence yields valuable preliminary information pertaining to the probable flowing-out characteristics and blush-resistance of the drying film. It is generally accepted that, other factors being constant, the blush-resistance varies inversely with the rate of evaporation of the solvents. Flow, although not a function of the volatility alone, is governed by it to a considerable extent. The maintenance of the proper balance between active solvents and diluents during the drying process is extremely important from the standpoint of film characteristics, and this is largely determined by the relative rates of evaporation of the active and inactive components of the solvent system.

The information derived from simple evaporation rate comparisons of solvents and solvent mixtures, although unquestionably of value in predicting the behavior of the finished lacquer in many important respects, is open to question from several angles. In the first place, as the test is usually conducted in the absence of nitrocellulose, plasticizer, or other film-forming ingredients, the effect of these nonvolatile constituents of the finished lacquer is not taken into account. Nitrocellulose preferentially holds certain solvents by virtue of solvation or association. This property tends to distort the normal vapor pressure relationships as determined for the components of the solvent system alone. Furthermore, mixtures of certain solvents may behave abnormally because of the formation of azeotropic combinations; so that the evaporation rate of the solvent mixtures is not always predictable from the behavior of the individual constituents. Also, some of the methods in general use in the industry for determining evaporation rates do not yield reliable and reproducible results.

In measuring any physical constant, whether for purely scientific or for industrial application, it is highly desirable, whenever possible, to express results in absolute units. Evaporation, however, is affected by such a variety of external variables that it is virtually impossible, where simplicity and speed are of prime importance, to establish sufficiently controlled conditions to allow absolute expression of results. Hofmann (*3*) expresses the evaporation rates of organic liquids in terms of the slopes of the evaporation rate curves, selecting *n*-butyl acetate as a standard of comparison and assigning to it an arbitrary value of 100. It is obvious that only pure liquids, the slopes of which are constant, can be satisfactorily treated in this way. In any case, the results, however expressed, are not reliable unless a method of determination is employed which will yield reproducible data.

The ideal method for measuring evaporation rates should provide for rigid control over many variables such as temperature, pressure, humidity, velocity of the air, and the amount of liquid surface exposed. A method described by Polcich and Fritz (*4*) takes these factors into account perhaps as well as any yet devised. Air of definite temperature and humidity is passed at a given rate over the sample of liquid contained in a flask maintained at a constant temperature. The volume of air required to evaporate the sample is used as a measure of the rate of evaporation. Careful standardization of the manner in which the air is led over the liquid is important, however, and the method offers the disadvantage that only one liquid can be studied at a time.

Realizing the impracticability of attempting to control all the variables encountered, lacquer technologists have endeavored to minimize their effect by resorting to a method whereby the evaporation rate of the solvent under investigation is determined simultaneously with that of some standard liquid. This allows a direct comparison which should not alter appreciably with moderate changes in conditions.

As usually carried out, this method consists of pipetting equal volumes of the standard and experimental solvents into uniform cups or pans of predetermined weight. The weights of the samples are then quickly determined to the nearest milligram, and the cups are placed close together on an exactly level platform where the solvents are allowed to evaporate under the prevailing atmospheric conditions of the laboratory. At intervals the samples are reweighed and the loss in weight and the time are recorded. The percentage evaporated versus the time is finally plotted on coördinate paper and the graph furnishes a convenient record of the desired comparison. To simplify weighing, several devices have been proposed, among which are the Jolly balance and the Hart balance (*2*). The latter employs an evaporation pan attached indirectly to a pointer, by means of which the weight evaporated can be read directly from a scale at any time during the course of the determination.

This general method, which may be called the "static method," although widely used, is far from accurate. Local temperature differences, inconsistent air currents, and stagnation of the solvent vapors over some of the cups (when a large number of comparisons are being made at one time) account for the major portion of the discrepancies observed. The use of guards for the purpose of minimizing the effect of air currents serves only to accentuate the stagnation effect which may be accompanied by a certain amount of condensation that is apt to occur in any partially enclosed space. Wilson and Worster (*5*) have attempted to improve upon this method by placing the evaporation cups in a tunnel through which air is forced by means of an electric fan. While this is a step in the right direction, it appears doubtful whether the velocity of the air is actually constant over the entire area occupied by the samples, especially when half a dozen or more liquids are being studied simultaneously.

Evap-O-Rotor

This brings us to a discussion of a device developed by the author for a more accurate determination of evaporation rates.

The instrument, which has been christened the Evap-O-Rotor, consists of a circular turntable 40.5 cm. (15 inches) in diameter rotating at a constant rate of 1 revolution per minute. The table is constructed of two parallel aluminum plates spaced about 1.25 cm. (0.5 inch) apart. Around the outer edge of the upper plate are ten equally spaced holes of suitable diameter to receive the evaporation cups and allow them to rest squarely on the level surface below. An adjustable circular guard about 15 cm. (6 inches) in height surrounds the rotating parts; this can be raised, lowered, or removed altogether as desired. Power is furnished by a 0.25-horsepower, vapor-proof, electric motor operating the table through a gear-reduction unit. The entire apparatus is mounted on a heavy iron base which is bolted to a bench in such a manner that the rotating table is in an exactly level position.

A convenient type of evaporation cup to use with this instrument is a flat-bottomed, straight-sided aluminum pan 2.5 cm. (1 inch) deep by 6.25 cm. (2.5 inches) in diameter. For accurate results it is important that the evaporation cups possess a high degree of uniformity. Slight variations in depth, small dents, or corrosion pits in the metal and in general any irregularity in the bottom of the cup will often disturb the rate of evaporation, particularly near the dry-point of the determination. Some investigators (*1*) prefer to use a cup with a very slightly concave bottom. This is advantageous in that the last traces of solvent tend to collect at the center instead of in the corners as sometimes occurs with the flat-bottomed type.

The procedure followed in carrying out the determination is essentially the same as that described under the static method.

Two to five cubic centimeters of liquid (depending on the vapor pressure of the material under test) are pipetted into the cups and, after weighing to the nearest milligram, these are placed in the depressions on the rotating table. The time is recorded as each successive sample is started, and at intervals the cups are reweighed in the same order that they were originally placed on the machine. A maximum of ten samples can be handled conveniently in this way.

The principle of the Evap-O-Rotor is simple and does not require a detailed discussion. Obviously the device does not actually control variable conditions in the laboratory, but its value lies in the fact that it distributes the effect of these variables evenly over all the samples under test and thus prevents any marked distortion of the comparative results. The rotary principle insures that all the cups are successively subjected to any local differences in air currents and temperature which may occur within the area occupied by them. The slow continuous motion is also effective in preventing stagnation of vapors over the evaporating liquids.

Comparative Tests

In order to test the efficacy of the instrument, numerous tests were conducted comparing the static and Evap-O-Rotor methods. The general procedure employed was to pipet exactly 5 cc. of pure toluene into each of ten standard evaporation cups and to record the total time required for each sample to evaporate. Obviously if the method used were ideal, these times would all be identical. Early tests using the static method showed variations from the mean time of more than 12 per cent in some cases. While it was possible by use of the Evap-O-Rotor to show that about one-fourth of this error could be attributed to slight inconsistencies in the cups used, recent tests conducted with highly standardized cups have confirmed the inaccuracy of the static method.

A typical test has been selected to illustrate the advantages of the Evap-O-Rotor over the older method. Twenty evaporation cups of high uniformity were selected and 5 cc. of toluene were pipetted into each. Ten of these were placed on the Evap-O-Rotor and the remainder were grouped close by on an exactly level platform. The samples were allowed to evaporate in the absence of any direct draft except for incidental air currents in the laboratory. Table I shows the results of this direct comparison of the two methods. While the maximum deviation from the mean by the static method is 5.4 per cent, the Evap-O-Rotor reduces this error to a maximum of 1.4 per cent.

Table I. Static Method vs. Evap-O-Rotor Method

(Test liquid, 5 cc. of toluene)

Static Method[a]			Evap-O-Rotor[b]		
Cup	Evaporation time	Variation from mean time	Cup	Evaporation time	Variation from mean time
	Min.	%		*Min.*	%
11	308	−5.4	1	306	−1.4
12	312	−4.2	2	309	−0.4
13	321	−1.4	3	312	+0.5
14	321	−1.4	4	312.7	+0.8
15	329.5	+1.2	5	310.5	0.0
16	331.5	+1.8	6	312.2	+0.6
17	327	+0.4	7	311	+0.2
18	334	+2.6	8	309.7	−0.2
19	343	+4.7	9	309.5	−0.3
20	330	+1.3	10	310	−0.1
Mean time 325.7			Mean time 310.3		

[a] Temperature, 24.5° to 25.5° C.
[b] Temperature, 23.5° to 25.0° C.

Whether the shield surrounding the turntable has any bearing on the accuracy of the results has not been determined. The principle on which the device is based, however, would indicate that the shield probably is not essential.

For determining the evaporation rates of solvents of low vapor pressure, it should be possible to employ an electric fan in conjunction with the Evap-O-Rotor. While the author has not experimented along this line, other users of the instrument report satisfactory results with such a combination.

Acknowledgment

In closing, the writer wishes to acknowledge the credit due J. P. Burke of the du Pont Parlin Laboratory, not only for his assistance in designing the Evap-O-Rotor but also for his coöperation in obtaining the data used in this paper.

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Photoelectric Photometers for Use in Colorimetry

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THE recent development of photoelectric cells (*9, 19, 28*) has made it possible to avoid many limitations that characterize the use of photometric colorimeters read by means of direct ocular observation. Some of the photoelectric photometers thus far described have single photocells (*1, 5, 6, 7, 10, 12, 14–18, 21*), while others (*2, 3, 4, 8, 11, 13, 20, 22*) have two. The two-celled form seems to the writer to be preferable. In this paper are described two newly developed instruments of the two-cell form, which have proved satisfactory for the determination of potassium, phosphorus, and arsenic in solutions (*24–27*).

In the first instrument two photoelectric cells are on opposite sides of the light source, and between light and photocell, on each side, are an adjustable diaphragm (from a Pulfrich photometer, made by Carl Zeiss, Inc.) and also a solution cell. While the two solution cells contain the same known solution, the diaphragms are adjusted so that the current output from both photocells is the same, as shown by means of a galvanometer. Then the known solution in one solution cell is replaced by the solution to be studied and the diaphragm on the opposite side is closed until the galvanometer again stands at zero. The reading for the unknown solution is taken from that diaphragm scale, which shows the amount of closure required to balance the two beams after the unknown solution is introduced.

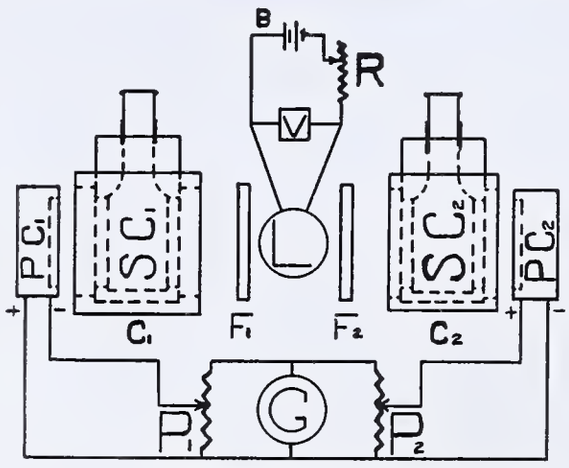

FIGURE 1. ARRANGEMENT OF PARTS OF TWO-CELL PHOTOELECTRIC PHOTOMETER WITH POTENTIOMETERS

L, light source
R, resistance (0.5 ohm)
V, voltmeter (8 volts)
B, heavy-duty battery (10 volts)
F_1, F_2, color filters
C_1, C_2, openings in cabinet, each with its own solution cell (SC_1, SC_2)
PC_1, PC_2, photoelectric cells
P_1, P_2, potentiometers with calibrated dials
G, galvanometer

The second instrument is like the first, except that adjustments and readings are made by means of calibrated potentiometers instead of diaphragms. Its essentials are shown in Figure 1

In building either of these photometers it is advisable first to decide upon the general arrangement of parts, including size of cabinet and distance from light source to photocells. Then a suitable light source and galvanometer are chosen and, finally, two photocells are selected, which have been matched by the manufacturer for the required light intensity, resistances, etc.

Set-Up of Photometer

Weston photronic cells, model 594, mounted firmly in the cabinet by means of UX-type radio sockets, have given excellent results. They are connected so that terminals of opposite polarity are joined, with the galvanometer in parallel with these cells; Wood (*23*) showed that this arrangement has advantages with respect to sensitivity, linearity of response, and stability, and it has been employed by Shook and Scrivener (*20*) and by Brice (*4*). The potentiometers are of the General Radio Company's type 374-A, each equipped with that company's No. 717-C calibrated dial and with a vernier added by the writer; it is desirable to choose the resistances so as to permit direct readings of light transmission (*4*). The light source is a single-filament, 6- to 8-volt Mazda bulb of the type used for automobile headlights, mounted on the rear wall of the cabinet so as to be midway between the two photocells. A large rectangular opening in the bottom of the cabinet beneath the bulb permits free air circulation around the latter, for the cabinet itself stands on four rubber knobs or legs about 1 cm. high. Ordinary house current, with or without transformer, proved unsatisfactory, notably because of fluctuating voltage, and a 10-volt battery was finally employed as current source. A voltmeter with capacity of 8 volts and a rheostat with capacity of 0.5 ohm are in series with battery and bulb, so that the light intensity may readily be kept constant.

Because the cement of cemented glass solution cells may be attacked by the solutions to be studied, specially blown flat-sided glass flasks were developed for the solution cells. The body of each flask is a horizontal cylinder about 5 cm. in diameter, with the ends closed. A vertical neck extends upward about 6 cm. from the cylindrical body. To permit different thicknesses of solution layer to be interposed between bulb and photocell, solution flasks with different lengths of cylindrical body (from about 1 cm. to about 6 cm.) are provided, holding about 10, 25, 50, and 100 cc. of solution, respectively. The necks of the larger flasks are about 1 cm. in diameter, but when the main cavity is less than about 1 cm. thick the neck is narrower.

Each flask is held in a rectangular case of Bakelite (or wood), the two like parts of which are screwed together after the flask is in place. Each part is provided with a circular window having the same diameter as the sensitive surfaces of the photocells. A rubber ring around the neck of each flask supports the flask in its case. All cases for the left side of the cabinet are alike in external size and shape but those for the right side, although also alike, are slightly different from those for the left side, and the two openings in the cabinet, which receive the cases, are correspondingly slightly different. This is because the flat sides of the flasks are not accurately plane, and consequently each flask must have its own position in the cabinet, either at left or at right. Light from the bulb shines horizontally through the cylindrical body of the solution flask to the photocell on the same side. When the light beam is to be shut off or narrowed, suitable blocks of Bakelite or wood, with or without circular openings, are employed as convenient diaphragms.

A calibration curve (*2, 12, 20*) is made from readings on a series of different known concentrations of the solute to be studied and readings obtained with unknown solutions of that solute are referred to that curve. When the unknown solution to be studied is slightly turbid or when its color tone is somewhat different from that of the standard solution series represented by the calibration curve, it is advisable

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to add (*2, 12, 20*) a known quantity of known standard solution and to compare the resulting mixture photometrically with another sample of the unmodified unknown solution.

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A Photoelectric Colorimeter

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During the past few years much interest has been taken in the use of photoelectric cells in photometric chemical analysis. The chief advantages are greater sensitivity and the elimination of errors due to eye fatigue and to the inability of the observer to judge color intensity accurately. Some of the colorimeters described in the literature use a single photocell, others employ two. The photometric balancing or comparison has generally been accomplished either by means of adjustable diaphragms and a galvanometer or by the use of a potentiometer. The chief objections to some of these colorimeters are their lack of compactness and portability and the need of expensive resistances, potentiometers, galvanometers, etc. The photoelectric colorimeter described in this paper (Figure 1) is a self-contained instrument of moderate cost and is the result of several years of investigation in this laboratory. During this time many arrangements of both the optical and the electrical systems were tried with varying success. The instrument herein described has proved very satisfactory.

Description of Apparatus

Photocell Circuit. Only one photoelectric cell is used and it is the photovoltaic type which acts as a source of current without the aid of an external e. m. f. The fundamental characteristic of this type of cell is the current, which is almost exactly proportional to the light intensity for low resistances in the external circuit, rather than the e. m. f. as is usual in the ordinary sources of electrical energy. The cell used here is a photronic cell, Model 594, manufactured by the Weston Electrical Instrument Corp. (*1*). It is connected in series with a microammeter (*MA*, Figure 2) having 50 ohms resistance and reading up to 50 microamperes. A special scale permits an accurate estimation to 0.1 microampere.

Light Circuit. The source of energy is a 6-volt, 17-plate lead storage battery and the lamp used is a 6- to 8-volt, single-filament auto headlight bulb. The lamp, *b*, is connected to the battery terminals through a pair of resistances, R_1 and R_2, in parallel, one for coarse and the other for fine adjustment. Across the lamp is connected a small voltmeter, *V*, reading up to 8 volts, for approximate adjustment of the resistances.

Optical System. Below the lamp is placed a spherical metal reflector, *a*, with the filament at its center of curvature, so that light rays are reflected back upon themselves to approximately double the intensity of the beam traveling upward through diaphragm, *c*, which defines the beam. Above the filament a lens, *d*—diameter, 2.5 cm.; focal length, 5 cm.—is placed at its focal distance, so that the beam striking it is rendered very nearly parallel. Another diaphragm, *f*, limits the parallel beam before it enters the tube containing the liquid. The unabsorbed light then strikes the surface of the photocell exposed by the aperture of diaphragm, *g*. The beam is rigidly defined in order to eliminate as far as possible errors due to stray reflections from the sides of the tubes, which are never entirely regular; condensing lens effect of drops at the tops of the tubes; reflections from finger prints on the outside of the tubes; and the diverging lens effect of the meniscus, an error which is here reduced to a minimum by having the diameter of the beam small in comparison with the diameter of the meniscus.

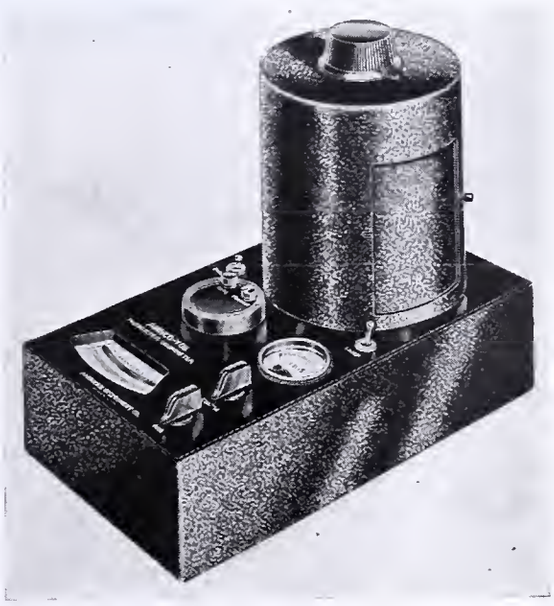

Figure 1. Photoelectric Colorimeter

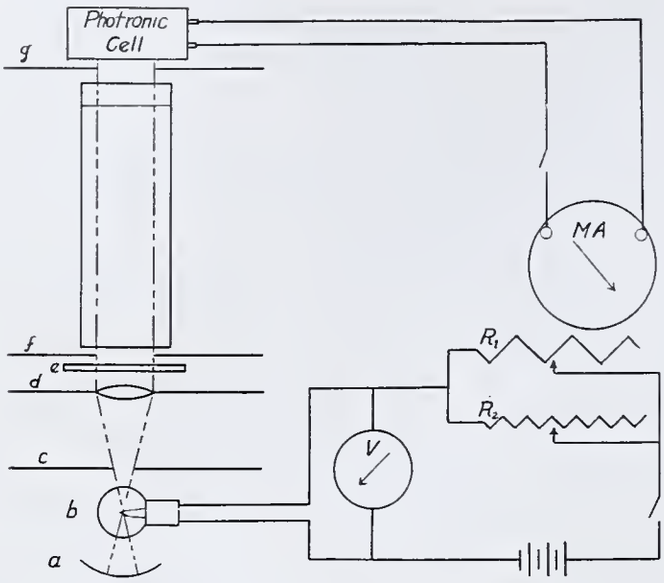

FIGURE 2. DIAGRAM OF APPARATUS

TUBES. The tubes (Figure 3) are made from precision-bore tubing of clear glass and have optically plane, fused-on bottoms to prevent distortion of the beam. The inside height to the graduation mark is 100 mm. and the volume is 100 ml. These tubes can be made so that the volume variation is a negligible fraction of a milliliter (100.04 ml. is the volume of each of the two tubes at hand). This provides a very convenient volume for ordinary work.

MECHANICAL CONSTRUCTION. On the bottom of each tube is cemented a brass ring into which a slot has been cut to coincide with a pin, so that the tube is always held in the same position. A turntable, mounted on smooth bearings, carries the two tubes and successively rotates them into position in the light path. A ratchet device with the two fixed points insures the correct position of the tube for a reading. At the base of the cylinder containing the turntable, a convenient slide permits the insertion of color filters just above the lens (*e*, Figure 2). When a filter is not used, a clear optical flat is kept in the slide to protect the lens and to keep out dust. A sliding door on the side of the cylinder opens to permit insertion of the tubes and when closed keeps out stray light and dust.

The lens, lamp, and reflector are all rigidly mounted in a light-alloy casting. The lamp socket is adjustable to permit accurate centering of the filament with respect to the lens, and the reflector can be focused by means of a screw, thus permitting realignment of the beam should a bulb have to be replaced.

A pair of adapters (Figure 3) can be mounted on the turntable, suspended from the shoulders that hold the tops of the large tubes in fixed position. The adapters hold microtubes (5 ml.) so that the instrument can be used in cases where only very small volumes of liquid are available, as is often the case in biochemical and biological work.

Operation

The first and a very important step is cleaning the tubes and securing a photometric balance. The tubes are first cleaned inside with sulfuric acid–dichromate cleaning solution and then rinsed very thoroughly with distilled water. The bottoms are occasionally washed with a soap solution free from abrasive, but ordinarily polishing them with lens paper is sufficient.

The tubes are filled to the mark with distilled water and then placed in position in the instrument. The sliding panel is closed and the light switch turned on. The coarse resistance is adjusted so that the voltage reading is approximately 3 volts. The instrument must then be allowed to stand for 2 or 3 minutes to permit the filament and the rheostats to warm up so that their resistance becomes fairly constant. Then the photocell switch is turned on and the intensity of the light adjusted by means of the coarse and fine resistances so that the microammeter reads 50 with tube I in position. Tube II is then quickly turned into position. The reading should be 50, when the needle has come to rest. It is necessary to turn I back into position to make certain that the reading is still 50. The first reading is the least reliable and in this work it was discarded and the mean of three readings on tube II, between which the readings on I did not vary from 50, was taken as the correct value. If an exact balance is not attained, for the sake of simplicity in handling the data, it is better to secure it by again polishing the bottoms of the tubes. The same procedure is followed in taking the reading of a colored solution in tube II. Tube I is filled with the blank solution and the microammeter always set at 50. By having the blank solution contain everything except the color-producing substance, errors due to the absorption of light by other substances in solution are automatically eliminated. Setting the light intensity to a definite value with the blank makes it unnecessary to have a sensitive voltmeter, since an exact knowledge of the voltage applied is not required.

The photronic cell has an inherent objectionable defect which may be classified as a "fatigue" effect, and can produce an appreciable error unless the proper care is observed in operation. When the cell is first exposed to light its reading is high, but after a very short time it drops to a constant value. As long as the solution is dilute and transmits almost as much light as the blank, the fatigue effect is negligible, but when the solution is concentrated, it is necessary to wait for about a minute before taking the reading of the blank. This delay may allow the voltage across the lamp to change, since the battery is continuously discharging and the reading may be in error by as much as 1 μa. This voltage change may be reduced greatly by using a battery with a high ampere-hour capacity or by using two batteries connected in parallel. However, for work of the highest accuracy, it is necessary to determine the approximate concentration of the unknown and then make up a standard of that concentration. Setting the light intensity to the correct reading of the standard, the reading of the unknown is taken and the relationship between the readings and the concentrations is given by Equation 5.

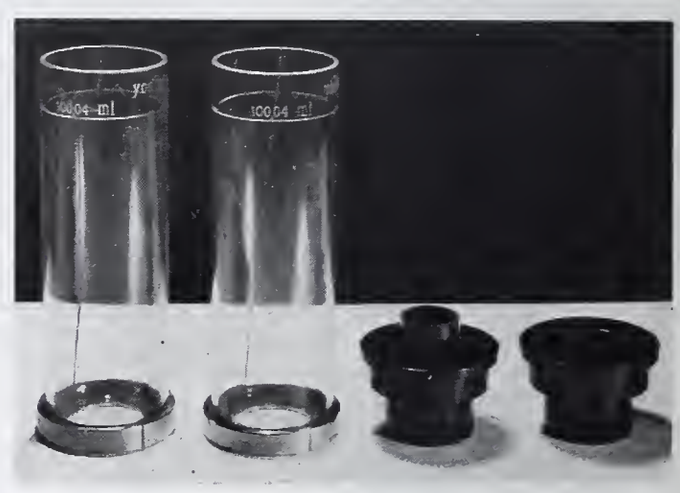

FIGURE 3. TUBES AND ADAPTERS

In case solutions to be studied must be made up with a colored reagent or contain colored substances which do not interfere by chemical reaction, color filters may be used to eliminate their absorption. If a color filter having the same spectrophotometric transmission curve as the interfering colored substance be inserted in the light path and the blank set to a reading of 50 μa as before, the absorption observed will be due almost entirely to the substance whose concentration is to be measured. It is thus unnecessary to know the concentration of the interfering colored substance so long as it remains below the limit of the depth of color of the filter.

When the microcells are used, the reading of the blank is set at 25 rather than 50 because a smaller area of the photronic cell is exposed and sufficient intensity to cause full scale deflection would discharge the battery so rapidly that constancy of the blank reading could be maintained only with great difficulty.

Calibration

The instrument must be calibrated for the quantitative determination of a substance by means of a given color reaction. Two methods may be used for handling the data, the choice depending upon the accuracy demanded and the time available. The first, and simpler, method is a plot of ammeter readings against concentrations (Curve I, Figure 4) or a curve of the decrease in ammeter readings against concentrations (Curve II, Figure 4) gives a positive slope

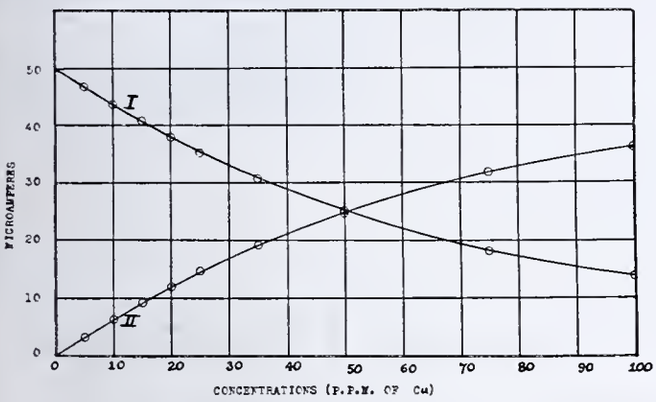

FIGURE 4. CALIBRATION CURVES

and may be preferable. In either case, the concentrations may be read directly from the graph. Using this method, however, precludes the possibility of eliminating the error due to the fatigue effect mentioned previously. The second method of handling the data is based on two assumptions: the validity of Beer's law and proportionality of current production to light intensity.

Beer's law in its most familiar form is:

$$I_c = I_0 \cdot 10^{-\alpha c x} \qquad (1)$$

taking logarithms

$$\log I_c = \log I_0 - \alpha c x$$

Assuming direct proportionality of current to light intensity,

$$R = KI \qquad (2)$$

where R is the ammeter reading. Since the depth of solution x is constant (100 mm.) α and x may be combined into another constant k

$$\log \frac{R_0}{R_c} = kc \qquad (3)$$

A plot of log R_0/R_c against c should give a straight line whose slope is k. That such is the case, at least within certain limits, can be seen from Figure 5. Plotting the curve and evaluating the slope makes it possible to calculate the concentration from the relation:

$$c = \frac{1}{k} \log \frac{50}{R} \qquad (4)$$

From this the relationship between two concentrations and their readings follows:

$$\frac{c_1}{c_2} = \frac{\log 50/R_1}{\log 50/R_2} \qquad (5)$$

A table of the values of log $50/R$ for values of R from 50 to 10 at intervals of one-tenth was made up and much time saved in the calculations.

The first step in studying a given color reaction is to determine what the blank solution must contain. It is advisable to choose a fixed amount of the color-developing reagent, or reagents, of sufficient quantity to give a large excess for all concentrations that will be encountered. If the excess be very large, the amount used up in the reaction will be negligible in comparison and the variation in percentage excess will be small, so that the system will more closely approximate Beer's law conditions. If the blank solution is found to show a measurable absorption, it must be used as the blank in tube I, but if it shows no absorption or a filter can be found which will match its absorption, distilled water may be used in tube I and thereby greatly simplify the procedure.

The colored solution on which the most extensive investigation was carried out was ammoniacal cupric sulfate [$Cu(NH_3)_4SO_4$]. It was chosen because it is a relatively poor colorimetric system for visual study and hence would give the instrument as rigid a test as possible and still remain within the limits where comparison with visual methods could be made. Ammonia solutions exhibit an appreciable absorption in the visible region; hence it was necessary to use as a blank an ammonia solution of the same strength as the standards in which an excess of very large magnitude was used. Less extensive studies on two other systems gave comparable results, so that the results which follow may be considered as typical, but it must be remembered that many colorimetric reactions give solutions of the order of one hundred times as intense a coloration at a given concentration and the sensitivity to concentration change is therefore of the order of one hundred times as great.

Results

The stock copper solution was prepared from reagent grade $CuSO_4 \cdot 5H_2O$ by dissolving 39.282 grams in a liter of solution at 20° C. Then 100 ml. of this solution were diluted to a liter to give a solution which contained 1 mg. of copper per ml.

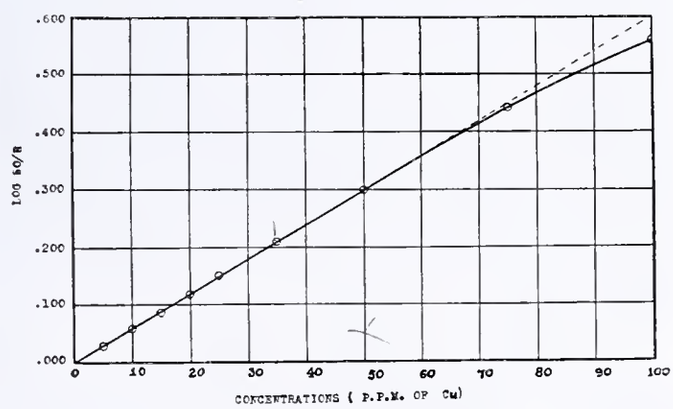

FIGURE 5. CALIBRATION CURVES

This was then checked by electrolytic deposition and was found to be exact. The test solutions were made up over a range of 5 to 100 p. p. m. of Cu^{++}, the proper number of milliliters of the Cu^{++} solution (1 mg. per ml.) being added to 25 ml. of 15 M ammonium hydroxide and diluting to a liter. Thus in the most dilute solution the amount of ammonia present was 1200 times that required for the reaction

$$Cu^{++} + 4\,NH_3 = Cu(NH_3)_4^{++}$$

and in the most concentrated, 60 times the theoretical amount. The blank was made by diluting 25 ml. of the same ammonium hydroxide solution to a liter.

Following the procedure outlined under "operation," the following results were obtained with the $Cu(NH_3)_4^{++}$ solutions of concentrations as indicated.

TABLE I

Copper, p. p. m.	R 1	R 2	R 3	R Mean	50-R	log 50/R
5	46.8	46.8	46.8	46.8	3.2	0.029
10	43.8	43.7	43.7	43.7	6.3	0.059
15	40.9	40.9	40.9	40.9	9.1	0.087
20	38.0	38.0	38.0	38.0	12.0	0.119
25	35.4	35.3	35.3	35.3	14.7	0.151
35	30.8	30.8	30.8	30.8	19.2	0.210
50	25.1	25.2	25.1	25.1	24.9	0.299
75	18.1	18.1	18.1	18.1	31.9	0.441
100	13.8	13.8	13.8	13.8	36.2	0.559

These data are plotted in Figures 4 and 5. From Figure 5 it can be seen that the linear relationship predicted by Equation 3 holds over a fairly wide range of concentrations, the value of k being 0.00599.

In repeating the above with two new sets of solutions, the values of k obtained were 0.00603 and 0.00597, respectively. A reliable average of these values is $k = 0.0060$.

A solution, whose concentration was unknown to the observer, was placed in tube II and gave a reading of 44.7 μa. From the curves of Figure 4, this means a concentration of 8.2 p. p. m. Or, the following calculation gives

$$c = \frac{\log 50/44.7}{0.0060} = \frac{0.0486}{0.0060} = 8.1 \text{ p. p. m.}$$

The correct concentration was 8.0 p. p. m. In comparison with visual methods, by means of Nessler tubes in a roulette comparator (*2*), a solution containing 8 p. p. m. can be distinguished only with difficulty from 7 or 9 p. p. m., and with certainty from 6 or 10 p. p. m.

Acknowledgments

The authors are indebted to Frederick L. Brown of the Rouss Physical Laboratory for many helpful suggestions and to Robert H. Kean of this laboratory for assistance in studying some of the early models of the colorimeter. Our thanks are due the American Instrument Company, Washington, D. C., for building the apparatus and for assistance in solving some of the problems of design.

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(2) Yoe and Crumpler, Ind. Eng. Chem., Anal. Ed., 7, 78 (1935).

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A Pressure Regulator for Vacuum Distillation

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A NUMBER of devices have been described in recent years for the control of pressure, the most recent being those of Palkin and Nelson (*2*) and Jacobs (*1*). The apparatus described below is very simple in construction and is rugged and foolproof. There are no ground joints subject to wear and leakage, no liquids likely to cause corrosion, no electrical contacts subject to disturbance, and no fragile glass parts which cannot be replaced in a very few minutes. The action of the regulator is not affected by traces of impurities in the mercury in the U-tube. The regulator is actuated directly by the vacuum itself without the aid of a secondary outside agency. The only wearing part requiring replacement is the rubber valve seat and this can be cut, without special tools, from any reasonably good rubber sheet.

This device is not intended to furnish extreme accuracy, but it will control pressures within the accuracy of laboratory thermometer readings over a wide range, with a minimum of attention in the way of adjustment and repairs.

While this regulator operates on the flutter-valve principle, the valve never shuts off entirely while in operation (except when the vacuum is first being built up), but the rubber valve seat "floats" an infinitesimal distance from the surface of the glass orifice. This makes for smooth operation.

In Figure I (a side elevation of the apparatus) A is a small square of sheet rubber cemented to a metal plate which in turn is riveted to lever C. B is a glass capillary tube about 4 cm. long and ground down to the edge of the orifice at its upper end. The lower end fits into pressure tubing held by clamp E, the position of which is adjustable by knurled nut G, and which is connected to the vacuum line preferably as near as possible to the distilling flask. When A closes down on B, the influx of air stops and the vacuum builds up, and vice versa. Lever C revolves on pivot F, and has attached to it a threaded stud carrying a counterweight, D, which serves as a fine adjustment for the valve assembly. The metal plate carrying A projects beyond the rubber square and engages a slot in metal bracket H. K is the main bracket which is bolted to an instrument board at L.

In Figure II (an elevation taken at right angles to that of Figure I) M is a wooden beam which swings on knife edge N, hung on bracket P, which is also bolted to the instrument board. To the wooden beam is attached U-tube Q, the horizontal portion and right leg of which consists of Pyrex capillary tubing of 3-mm. bore and is sealed at the end, like a closed-end manometer. The left leg consists of Pyrex tubing of 5-mm. bore and is attached to the vacuum line by means of a piece of pure gum tubing filled with short glass cylinders to prevent its collapse under vacuum, and at the same time allowing the greatest possible degree of flexibility. Sensitivity can be increased somewhat by increasing the difference between the bores of the two legs of the U-tube. The U-tube is filled with mercury for the full length of the 3-mm. capillary.

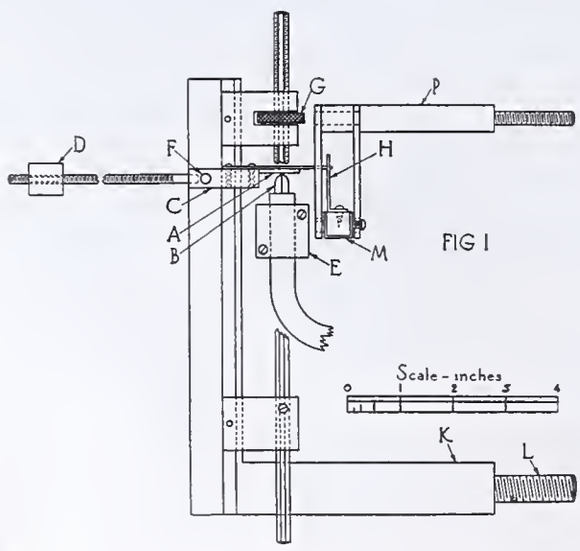

FIG I

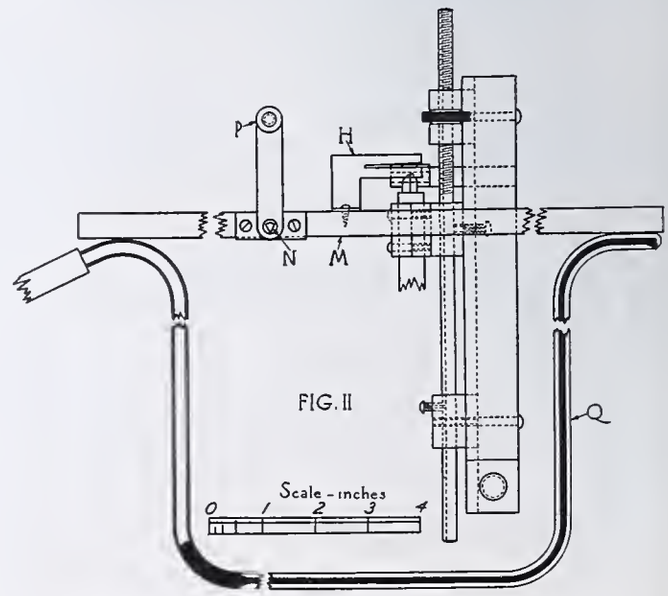

FIG. II

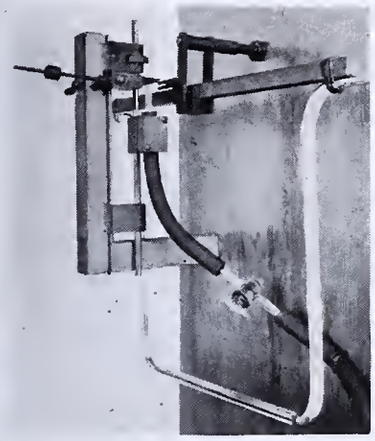

FIGURE III. PHOTOGRAPH OF APPARATUS

This apparatus will control the pressure within 1 mm. and its over-all range is limited only by the depth of the U-tube, up to 760 mm. In order to set the regulator for the required pressure, the position of the U-tube with respect to knife-edge *N* is first adjusted by sliding beam *M* through the sleeve by means of which it is attached to the knife-edge *N* until approximately the required pressure is obtained in the system as measured by an independent manometer. When the required pressure is on the system, beam *M* should be in an approximately horizontal position. Further adjustment is obtained by means of *G* and the final regulation may be controlled by means of *D*.

The operation of the assembly is as follows:

As the air is exhausted from the system, the mercury in the U-tube is drawn up in the left leg only a fraction of the distance which it drops in the right leg; hence a maximum weight of mercury crosses the center of gravity and causes beam *M* to swing on the knife-edge in such a way as to raise the rubber valve seat, thus allowing air to bleed in through *B*. As the vacuum decreases the beam swings back tending to close *B*. Actually, in operation, the rubber face on the plate attached to lever *C* floats an infinitesimal distance away from *B*, never actually shutting it off. This results in very smooth operation, as evidenced by the fact that the oscillation in mercury meniscus of the manometer approaches the limits of ordinary vision.

The size of the bore in capillary *B* should be chosen rather larger for low vacuums than for higher vacuums. A little experience will suggest the size of aperture to use in order to obtain maximum sensitivity.

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RECEIVED March 4, 1935.

Determination of Lead

Removal of Bismuth Interference in the Dithizone Method

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IN ANALYZING biological materials such as blood, excreta, tissues, etc., for their lead content by a previously described dithizone method (*1*), bismuth, if present, seriously interferes, inasmuch as it reacts with the dithizone reagent under the same conditions as specified for lead. Bismuth may often be present in specimens of this kind as a result of previous medication. In order to extend the applicability of the dithizone method for lead to materials also containing bismuth, the procedure described below was developed and incorporated in the original method. Bismuth is separated from the lead before its final estimation by extracting a nitric acid solution of the two metals, which has been adjusted to pH 2.0, with a chloroform solution of dithizone. Whereas lead does not react and remains in the aqueous phase, bismuth reacts with the dithizone reagent and forms a chloroform-soluble organic complex. By means of this additional step, amounts of lead ranging from 0.002 to 0.200 mg. have been satisfactorily recovered from samples of lead and bismuth nitrates containing 0.500 mg. of bismuth. Larger quantities of both lead and bismuth could, in all probability, be handled with equally good lead recoveries.

Procedure

GLASSWARE AND REAGENTS. These are the same as previously specified (*1*), with two exceptions. The concentration of dithizone solution 1 may be increased to facilitate the separation of appreciable quantities of bismuth. The solution should not be so concentrated, however, as to mask the color changes during extractions. With 0.50 mg. of bismuth, for example, a solution containing 0.20 gram of dithizone per liter is suitable.

Secondly, another indicator, acid *m*-cresol purple, standardized 0.04 per cent solution, is required.

PREPARATION OF SAMPLE AND SIMULTANEOUS EXTRACTION OF LEAD AND BISMUTH. The destruction of organic matter, the removal of lead and bismuth simultaneously from the digest with dithizone solution 1, and the conversion of the lead and bismuth from dithizone complexes to the corresponding nitrates is carried out exactly as described in the original method (*1*).

SEPARATION OF BISMUTH. Two drops of acid *m*-cresol purple are added to the nitric acid solution, which is then adjusted to pH 2.0 by the addition of 5 per cent ammonium hydroxide. At this point the solution should have a volume of 25 to 35 ml. The solution is extracted with 25 ml. of dithizone solution 1. Inasmuch as the reaction between an appreciable amount of bismuth and dithizone is rapid, the separatory funnel need not be shaken vigorously for more than 2 minutes. After complete settling, the chloroform phase is removed and discarded, 0.2 to 0.4 ml. of the chloroform solution being left in the separatory funnel, to guard against any loss of the aqueous phase.

The aqueous solution is reëxtracted twice more with 5-ml. portions of the dithizone solution. In each of these extractions the separatory funnel is shaken vigorously for 5 minutes to insure the removal of the last traces of bismuth. With 0.5 mg. of bismuth, the first portion (25 ml.) of dithizone solution is changed to a deep wine-red color by the reaction, the second portion (5 ml.) shows little, if any, color change, and the third portion (5 ml.) remains entirely unchanged in color; this indicates that the removal of bismuth is complete. Whether or not a color change has occurred is more easily observable during the shaking of the separatory funnel than after the subsidence of the chloroform phase. Larger amounts of bismuth would be removed in like manner by extracting with successive increments of the dithizone reagent until a newly added portion undergoes no change in color. Following the bismuth removal, the aqueous phase is

TABLE I. DETERMINATION OF LEAD IN SOLUTIONS CONTAINING 0.5 MG. OF BISMUTH AS THE NITRATE

(In these experiments the lead, as lead nitrate, was added by another chemist in amounts unknown to the analysts.)

Lead Added	Total Lead Found	Lead Found in Blank	Added Lead Recovered	Error
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
0.002	0.004	0.002	0.002	0.000
0.005	0.008	0.004	0.004	−0.001
0.008	0.010	0.002	0.008	0.000
0.023	0.024	0.002	0.022	−0.001
0.060	0.062	0.002	0.060	0.000
0.100	0.103	0.002	0.101	+0.001
0.110	0.113	0.004	0.109	−0.001
0.150	0.152	0.002	0.150	0.000
0.160	0.162	0.003	0.159	−0.001
0.170	0.171	0.002	0.169	−0.001
0.180	0.181	0.002	0.179	−0.001
0.190	0.193	0.003	0.190	0.000
0.190	0.192	0.003	0.189	−0.001
0.200	0.201	0.002	0.199	−0.001
0.200	0.203	0.003	0.200	0.000

washed with small portions of chloroform to remove the dithizone completely. A chloroform trap must be maintained continuously.

LEAD ESTIMATION BY TITRIMETRIC EXTRACTION. The aqueous lead nitrate solution is now ready to be prepared for the titrimetric extraction in which the lead content is determined. Two to three drops of phenol red, standardized 0.02 per cent indicator solution, and 2 ml. of 10 per cent potassium cyanide solution are added and the pH of the resulting solution is adjusted to 7.5 with 5 per cent nitric acid. (The residual *m*-cresol purple does not interfere.) The solution is then extracted with standardized dithizone solution 2 as described previously (*1*). As in the original method, combined reagent blanks, consisting of the same amounts of all the reagents used in the analysis, are carried along simultaneously with the sample and in identical apparatus in order to correct for lead added from this source.

Experimental Results

The data in Table I are representative of the results obtained. It is evident that the separation of bismuth does not affect the accuracy with which lead is recovered by this method.

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Permanent Aqueous Microscopic Mounts

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RESEARCH and instruction in many branches of the biological sciences call for microscopic examination of specimens of materials, many of which have to be in aqueous mountings. The lack of a quick and easy means for preparing permanent mounts of such specimens has made it impractical to assemble sets of standard slides for comparison, exhibition, and instruction, and has also delayed work in the field of microscopic study of slow reactions *in situ*.

The need has been for a suitable sealing material to prevent evaporation. The desired preparation must adhere tenaciously to smooth glass surfaces, flow freely into place, not dissolve or diffuse in water, not dry out or crack on long standing, and be firm enough to hold the mount in place. Many products were tried, such as Canada balsam, shellac, rubber, cement, beeswax, Halowax, asphaltum, glycerol-gelatin compound, etc., but each one failed to have all the necessary properties.

Finally the suggestion of Parker (*1*) led to the right combination. Wool fat (lanolin) is a sticky animal wax, but being rather soft it has to be hardened somewhat. The sealing material recommended is made by heating anhydrous wool fat (adeps lanae, U. S. P.) with not more than 20 per cent of rosin, until the constituents are blended. (A few minutes over a Bunsen flame are sufficient.) This mixture is firm at ordinary temperatures but on being heated it becomes liquid. It contains no volatile solvent and quickly congeals to hold the mount in position.

Any microscopic mount may be preserved by sealing the edge of the cover slip with the melted wax. The space under the slip should be filled with liquid, although a few air bubbles do not interfere with the permanence of the seal. The slide and cover slip should be dry at the points where the wax is to be applied. The melted wax may be applied with a thin glass rod or small brush, care being taken to have the wax come on top of the slip all the way around. Unless the slide is intended for the study of progressive reactions of reagents, growth of microörganisms, etc., the water used in their preparation should contain about 0.2 per cent by volume of 40 per cent formaldehyde solution.

A number of uses for such permanent mounts have come to the author's attention. A series of slides showing successive stages of a biological process may be prepared for classroom instruction, and once prepared they are available at all times. Preparation of such slides may be made part of students' laboratory work, and excellence of technic encouraged by making the best slides a part of the permanent collection.

Special or abnormal tissues may be kept for reference and further study. Observations by one investigator concerning a particular tissue may be reviewed by another investigator in some distant laboratory more understandingly if the comments of both are directed toward the same tissue on a permanent mount which is sent from one to the other.

Research workers may be able to follow with the microscope the slow reaction of a reagent on a biological tissue, diffusion through the walls of unbroken cells, the growth and multiplication of microörganisms, or the growth of crystals. The same microscopic structure may be examined at intervals over a period of days, weeks, or months.

An application of the use of permanent slides for instruction purposes was developed by Wildman (*2*) in connection with the Howard mold-count method for tomato products. He found it necessary to devise two additional features: (1) the thickening of the sample so that the filaments would not change position on the slide; and (2) the designation of specific fields on the slide for examination. The sample was thickened by stirring into the hot sample about one-third its volume of hot 3 per cent agar solution. The particular fields to be examined were designated by a pattern made by punching in thin transparent colored Cellophane 25 holes, each exactly the diameter of the microscopic field. This pattern was first mounted in balsam on the slide beneath a cover slip and the prepared sample was spread on top beneath a second cover slip and sealed.

Wildman used balsam for sealing the mount, but this is difficult to apply, slow to harden, and the seal is not always permanent. The wax described above has been used with entire satisfaction in the preparation of a number of such slides for the Howard mold-count method. An additional operation has been included in the examination of these slides which increases their usefulness for instruction purposes: A special reporting sheet having 25 circles each about 1 inch in diameter, arranged in the same order as the holes in the pattern, is used to record the observations of each observer. The analyst sketches in each circle a representation of the relative position and size of each piece of mold he finds in the corresponding microscopic field. After each analyst has recorded his observations on a separate reporting sheet, the results may be reviewed and further examination made of particular filaments.

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HARRISON E. HOWE, EDITOR

Quantitative Spectrographic Determination of Lead in Biological Material

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A quantitative spectrographic method for the determination of lead in various types of biological materials is described, in which the quantities of lead introduced into an arc are measured microphotometrically in terms of relative lead-line intensities. Some typical results obtained with known amounts of lead demonstrate an accuracy of ±0.00002 mg. for amounts of 0.00002 to 0.0004 mg. of lead within the arc. The influence of certain variations in composition of samples is illustrated, and other principal sources of error are mentioned.

AN EARLIER paper (*1*) from this laboratory described a spectrographic method for the quantitative determination of lead in urine. This method depended upon the measurement of the lengths of the wedge-shaped lines produced on a photographic plate by the interposition of a rotating logarithmic sector (*9*) between the arc and the spectrograph slit. The use of a microphotometer to measure line intensities has increased the accuracy and flexibility of the method, thereby justifying a description of the technic as it has been applied to the analysis of a wide variety of biological materials.

Apparatus

The spectrograph and accessory apparatus have been described previously (*1*). A Bausch and Lomb microphotometer of recent design was employed to measure the line intensities.

Calibration Curves

Unknown quantities of dissolved lead which are to be determined spectrographically must obviously be compared with known quantities of lead in solutions of like composition (within certain limits) with respect to the variety and concentration of the associated salts. The lead may be removed from the solution of any ashed biological sample as the sulfide, and added to a standard salt solution which is used to make up the known lead standards. Such a procedure has the advantage of its general applicability, but is to be avoided in dealing with the minute quantities of lead which occur in biological material, since the manipulations entail unavoidable loss of lead and increase the likelihood of contamination. Moderate variations in the composition and concentrations of the associated salts do not cause significant variations in results (Table I), and it is best, when feasible, to minimize the manipulation of samples by adapting the standard lead solutions so as to bring them into approximate correspondence with the samples, with respect to their salt composition. The various types of samples met with in general work may be separated for practical purposes into three groups, the analysis of which necessitates the use of separate lead standards and separate calibration curves.

Each working curve (Figure 1) was drawn from the data obtained from ten plates, each of which showed five spectra of 0.2-cc. portions of each of three lead standards. The mean values for the intensity ratios—Pb line λ2833.2/standard of intensity (Biλ2898.1) *2, 3, 7*—for each standard were plotted against the corresponding lead concentrations and the corresponding amounts of lead introduced into the arc. The three standards for curve I contained, respectively, per 100 cc. of solution, 0.01, 0.10, and 0.20 mg. of lead, 1 mg. of bismuth (the "internal standard", *7*), and the quantity of salts present in the ash of 1 liter of average normal urine.

A concentrated stock solution employed for making the standards for curve I and also for use as a diluent for certain samples, as indicated later, was made by dissolving the following salts: 170.5 grams of sodium chloride, 63.5 grams of potassium chloride, 31.5 grams of calcium chloride ($CaCl_2.6H_2O$), 20.0 grams of magnesium chloride ($MgCl_2.6H_2O$), and 37.5 grams of sodium dihydrogen phosphate ($NaH_2PO_4.H_2O$), in 1 liter of distilled water. After gassing with hydrogen sulfide and filtering to remove lead, the filtrate was acidified with triple-distilled hydrochloric acid (silica still), boiled to expel hydrogen sulfide, and made up again to 1 liter with triple-distilled water. Each 50 cc. of this solution contained sodium, potassium, calcium, magnesium, and phosphorus in amounts corresponding to those found in the ash of 1 liter of normal urine (*6*). (Sulfur was purposely omitted, since its presence or absence was found to be without effect upon the spectral intensity, within the limits of the concentrations employed.)

The standards for curve II differed from those for curve I only in that each contained 50 mg. of iron per 100 cc. (the amount present in 100 cc. of blood). This modification followed from the observed influence of iron upon the lead-line intensity (Table I).

The stock solution used in association with curve II was prepared just like that for curve I except for the final addition of 1.00 gram of iron in the form of pure iron wire.

The standards for curve III contained the metals present in the ash of 1 kg. of mixed food, in addition to lead and bismuth in the previously indicated quantities. This type of standard, and the resultant curve, were found to be necessary in dealing with large composite food samples with their relatively high phosphorus and potassium content.

The stock solution for making the standards and for use as a diluent was made by dissolving 58.9 grams of calcium chloride, 113.6 grams of magnesium chloride, 37.2 grams of sodium chloride, 174.4 grams of potassium monohydrogen phosphate (K_2HPO_4), and 12.2 grams of potassium chloride, in 1 liter of distilled water. After removing the lead by gassing with hydrogen sulfide and filtering, the filtrate, acidified with hydrochloric acid, was boiled to expel hydrogen sulfide, 0.48 gram of iron as pure wire was added, and the volume was brought up to 1 liter with triple-distilled water. Each 50 cc. then contained the amounts of sodium, potassium, calcium, magnesium, phosphorus, and iron which had been calculated from Lusk's data (*4*) as present in 1 kg of average mixed food materials.

Table I. Effect of Variations

Variation from Standard[a]	Ratio Found	Lead from Standard Curve	Ratio Found	Lead from Standard Curve	Ratio Found	Lead from Standard Curve
		Mg.		*Mg.*		*Mg.*
One-half average concentration	0.51	0.01	1.66	0.10	2.76	0.20
Twice average concentration	0.49	0.01	1.46	0.09	2.90	0.20
None	0.39	0.01	1.68	0.10	2.93	0.20
100% increase in NaCl	0.48	0.01	1.69	0.11	3.05	0.21
Potassium absent	0.40	0.01	1.61	0.10	2.69	0.18
100% increase in potassium	0.51	0.01	1.70	0.11	2.63	0.18
Phosphoric acid absent	0.55	0.02	1.60	0.10	2.63	0.18
300% increase in phosphoric acid	0.53	0.01	1.56	0.10	2.16	0.14[b]
Calcium absent	0.39	0.01	1.45	0.09	2.75	0.19
100% increase in calcium	0.53	0.02	1.65	0.10	2.74	0.19
Magnesium absent	0.35	0.01	1.58	0.10	2.83	0.19
100% increase in magnesium	0.55	0.02	1.81	0.11	2.65	0.18
Sulfuric acid absent	0.39	0.01	1.68	0.10	2.93	0.20
Addition of sulfuric acid (7.5 grams)	0.55	0.02	1.71	0.11	2.55	0.17
100% increase in NaCl and 50% decrease in potassium	0.33	0.01	1.64	0.10	2.80	0.19
100% increase in potassium and 50% decrease in NaCl	0.62	0.02	1.61	0.10	2.73	0.18
100% increase in NaCl and 50% decrease in phosphoric acid	0.53	0.02	1.56	0.10	2.70	0.18
100% increase in phosphoric acid and 50% decrease in NaCl	0.54	0.02	1.52	0.09	2.56	0.17
Standard plus 50 mg. Fe	0.50	0.01	1.60	0.10	2.42	0.16[c]

[a] Mean values for calibration curve I:
0.01 = 0.47 ± 0.01, standard deviation ± 0.10
0.10 = 1.61 ± 0.015, standard deviation ± 0.15
0.20 = 2.95 ± 0.024, standard deviation ± 0.25
[b] From 15 spectra. [c] From 30 spectra.

Curve I was used in the analysis of urine, bone, fat, nervous tissue, spinal fluid, and individual food samples or others low in iron; curve II for the analysis of blood, liver, spleen, heart, muscle, and individual foods or other samples which contained appreciable amounts of iron; and curve III for the analysis of large composite samples of food.

Preparation of Samples for Arcking

Urine. Samples were prepared as previously described (*1*), except that 0.1 mg. of bismuth per 10 cc. of final volume was used as the internal standard.

Other Biological Samples. Individual items of food (but not mixed food samples), blood, and animal tissues with the exception of bone, were digested with sulfuric acid and triple-distilled nitric acid in quartz Kjeldahl flasks, and evaporated to dryness. Because of their high calcium content bone and feces were ashed in a muffle furnace at 500° C., the former having undergone an initial digestion with triple-distilled nitric acid. The ash of each sample was dissolved in triple-distilled hydrochloric acid and the final volume was adjusted by dilution with triple-distilled water; the solution of bone was made to contain the ash of 1 to 5 grams of bone per 100 cc., that of blood the ash of 1 gram of blood per 1 cc., and that of other samples excepting feces, the ash of the entire sample (up to 100-gram sample) per 100 cc.; in the case of feces, the adjusted solution contained 1 gram of ash per 100 cc.

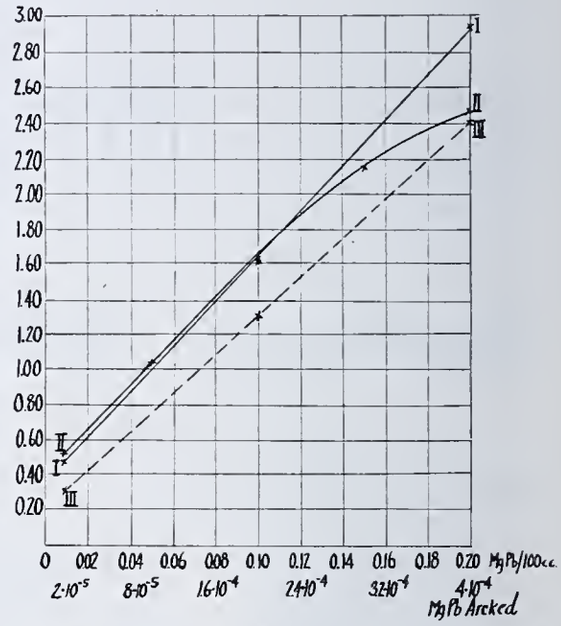

Figure 1. Variation of Intensity Ratios $\frac{Pb\lambda 2833.2}{Bi\lambda 2898.1}$ with Lead Concentration

These materials, to which none of the calibration curves applied directly, were adapted to analysis with either curve I or curve II by the admixture of their dissolved ash and the "lead-free" stock solution used in the preparation of the standards for curves I and II, as follows: Two cubic centimeters of the solution of the sample and 2 cc. of the appropriate stock salt solution (to which had been added 1 mg. of bismuth per 100 cc.) were introduced into 15-cc. Pyrex centrifuge tubes and concentrated to 2 cc. Each 0.2 cc. arcked then contained approximately 35 mg. of the inorganic salts of the stock solution plus a minute and practically unimportant quantity of ash derived from the sample. ("Lead-free" stock solution is one that has been treated previously with hydrogen sulfide and contains not more than 0.002 mg. per 100 cc. The quantity of lead in a few cubic centimeters of such a solution may be ignored since the lowest lead standard contains 0.01 mg. per 100 cc.)

Spinal Fluid. To 10 cc. of spinal fluid in a small quartz dish were added 2 cc. of triple-distilled nitric acid. After evaporating to dryness, the residue was ashed in a muffle furnace. The ash was taken up in a few drops of triple-distilled nitric acid and a little triple-distilled water, rinsed into a 15-cc. Pyrex centrifuge tube, and evaporated to 2 cc. in the water bath after the addition of 2 cc. of the stock solution used for the standards of curve I (to which had been added 1 mg. of bismuth per 100 cc.). Each 0.2 cc. then represented 1 cc. of spinal fluid.

Mixed Food Samples. Composite food samples were digested with nitric acid and ignited in a muffle furnace at a temperature of 500° C. (High-grade nitric acid without redistillation and Pyrex glass vessels may be used here. The contamination from their use is insignificant, in view of the considerable amounts of lead usually present in food.) The residue was dissolved in the least sufficient amount of triple-distilled nitric acid and triple-distilled water, transferred to a graduated glass stoppered 100-cc. Pyrex cylinder, and filtered if necessary to remove carbon. The proper amount of bismuth was then added and the volume of the solution adjusted so that 1 to 1.5 grams of ash were present in each 10 cc. of solution. Each 0.2 cc. of the solution then contained 20 to 30 mg. of inorganic salts.

Spectrographic and Photometric Technic

Employing successively the same 0.1-cc. capillary pipet, 0.2 cc. portions of the prepared solutions were placed in the crater of electrodes (7 mm. Acheson regraphitized graphite, 40 mm long with a crater 3 mm. wide and 10 mm. deep). After drying for several hours at 48.89° C. (120° F.) the electrode with the crater was made the negative, and for each such electrode a fresh electrode was made the positive in the arc. The electrodes

properly centered, were separated 5 mm. and the arc was started by momentarily bridging the gap with a graphite rod. Three-minute exposures were provided with an arc of 10 amperes and a 60-volt drop across the terminals. After passing through a quartz condensing lens the radiations, reduced 50 per cent by a rotating sector, fell on a slit 5 mm. long and 0.04 mm. wide. This procedure yielded a light background on the photographic plate, as well as lines of such width and length, when projected, as to cover completely the slit of the microphotometer. Five spectra of each of three samples were photographed on each plate (10 × 25 cm., 4 × 10 inches, Eastman No. 33). The plates were developed for 7 to 8 minutes at a temperature of 16.67° C. (62° F.) in a mechanically agitated bath of alkaline-hydroquinone developer, which was changed for each plate. After fixing (15 minutes) and washing (30 to 45 minutes) the developed plates were wiped gently with clean chamois and dried at room temperature for several hours.

Microphotometer measurements were carried out on thoroughly dried plates only. The throw of the galvanometer for the emulsion adjacent to each line was taken as the zero reading and the differences between these readings and those for the lines themselves were recorded as the line intensities. The ratio, reading for Pb line λ2833.2/reading for Bi line λ2898.1, was then recorded for each spectrogram. The value for the average ratio of the five spectra of each sample was then interpolated from the appropriate standard curve (Figure 1).

Discussion

In Table II are recorded the results obtained with known quantities of lead added to standard stock salt solutions. Although the repeated observations yielded identical results in several instances, successive spectra of the same sample may vary as much as 20 per cent. The lack of closer agreement is due primarily to the method of excitation employed. The arc between graphite electrodes has a tendency to wander and it is almost impossible therefore to obtain identical excitation conditions for successive spectrograms. The stability of the arc may be increased to some extent by reversing the polarities of the electrodes (*5*), as compared with the usual procedure, and by arcking relatively large quantities of material, 15 to 50 mg. If the arc begins to wander, however, it becomes very difficult to center it on the slit, and if most of the wandering occurs while either the lead or the bismuth is being volatilized into the arc the spectrogram will not correspond to those of the same sample which were made when the arc was consistently centered. The increased accuracy which results from the use of the average value from a number of spectra of the sample is illustrated in Table II. In general the averages of five observations give results which rarely vary as much as 0.01 mg. from the amounts known to be present.

The data of Table I show that variations in the concentrations of iron and phosphates result in significant variation in the values obtained for lead concentrations above 0.10 mg. of lead per 100 cc. This variation is remedied, in the case of iron, by applying the special curve derived for the analysis of iron-containing samples. When appreciable quantities of phosphoric acid occur in samples (easily determined from the intensities of the phosphorus lines on the plate), the sample should be diluted with stock salt solution in order to bring the amount of lead below 0.10 mg. per 100 cc. and thus to permit the application of the lower and more stable part of the curve. Occasional samples contain bismuth in such amounts as to exclude its use as the internal standard. Such samples may be analyzed without the use of the internal standard by a procedure similar to that previously described (*1*).

The principal sources of error, other than the factors cited above, arise from contamination of the sample during the process of collection and preparation. All vessels employed must be cleaned with hot nitric acid, followed by hot triple-distilled water, before each period of use. Samples once started should be carried to completion as rapidly as possible to avoid possible contamination. Various other opportunities for contamination have been discussed (*8*).

Table II. Results with Known Quantities of Lead

Pb Added *Mg.*	Curve Used	Mean Value	Ratio Pb/Bi	Pb Found *Mg.*	Pb Recorded *Mg.*
			0.42	0.01	
			0.44	0.01	
0.01	I	0.47	0.52	0.02	0.01
			0.54	0.02	
			0.42	0.01	
			Av. 0.47		
			1.04	0.06	
			1.06	0.06	
			1.00	0.05	
0.05	II	0.98	1.05	0.06	0.06
			1.13	0.06	
			1.05	0.06	
			Av. 1.07		
			1.52	0.09	
			1.42	0.08	
0.10		1.61	1.75	0.11	0.10
			1.56	0.10	
			1.70	0.11	
			Av. 1.59		
			1.64	0.10	
0.12	I	1.75	1.79	0.11	0.11
			1.84	0.12	
			Av. 1.75		
			1.59	0.10	
0.12	I	1.75	1.79	0.11	0.11
			1.70	0.11	
			Av. 1.70		
			2.86	0.20	
			2.86	0.20	
0.20	I	2.95	2.89	0.20	0.19
			2.79	0.18	
			2.68	0.18	
			Av. 2.81		

In dealing with biological materials the choice of lead line is limited to the most persistent line (λ2833.2) since it is frequently the only line to appear. With amounts of lead ranging from 0.00002 to 0.0004 mg. (0.01 to 0.20 mg. per 100 cc.) in the arc, the intensities of the lead lines produced in the photographic plate are such as to fall on the initial part of the blackening curve for the line λ2833.2. In this region the proportionality between the intensity (blackening) of the line and the intensity of radiation (concentration of lead) is more nearly expressed by the approximate formula

$$\text{blackening} = \text{constant} \times i$$

than by

$$\text{blackening} = \text{gamma} \log i/i_0$$

which holds for the straight-line portion of the blackening curve (*3*, page 14). It is more practical and convenient, therefore, to plot the intensity ratios against concentration instead of log concentration, in the development of standard calibration curves for the range of concentration dealt with herein. Lead concentrations above the range to which the curves apply may be adapted by dilution with the appropriate solution of salts; otherwise it is necessary to apply the observed data to calibration curves which are based upon relationships obtaining at a higher range of lead concentrations.

Summary

The technic as described has the following advantages over a method described in an earlier paper (*1*):

It has an accuracy of ±0.01 mg. over the entire range of applicability—i. e., for amounts of lead between 0.01 and 0.20 mg.

It permits the use of a single set of standard calibration

curves for interpolation of results, thus saving the time and plates required for making individual curves from the results on each plate.

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Volumetric Determination of Evaporation Rates

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THE development of modern protective coatings, particularly since the introduction of many of the now common synthetic resins, has emphasized the importance of the evaporation rates of the solvents and thinners used in their manufacture and application. A greater variety of materials, a more rigid control of finished product properties, and the development of fast-drying enamels have all been contributing factors.

All of the present methods for determining evaporation rates with which the authors are familiar are gravimetric. In the usual procedure 1 to 2 grams of the liquid are placed in a tared dish such as a friction-top can cover and weighed at intervals during the period of evaporation. Those which employ a special balance with sample suspended, thus doing away with tedious analytical weighings, are open to the criticism that only one or two samples can be measured at a time. Perhaps the best known of these special instruments is the Hart evaporation balance (*2*), a device equipped for one sample. Another special instrument, the Jolly balance (*3*), is equipped for two samples but, according to the method, requires a determination of a standard at the same time as the sample. It would be necessary, therefore, to use several units of these special instruments in order to conduct a number of tests at one time, thus involving a considerable investment in equipment.

Another difficulty encountered with most gravimetric methods is the control of air flow over the exposed area of the sample. Wilson and Worster (*6*) attempted to overcome this feature by the use of a special tunnel in which the samples are placed and through which a constant flow of air is conducted. This procedure, of course, requires manual analytical weighings at intervals, and is one of the things which the special balances, such as the Hart and the Jolly, overcame by making the weighings automatic. Also in the Wilson and Worster method it is admittedly difficult to control the current of air with a good degree of accuracy. Another device recently announced by Lowell (*4*), called the Evap-O-Rotor, requires the usual analytical weighings. It employs a turntable with capacity for several samples, the table being protected by a shield several inches high to minimize the effect of stray air currents. The table slowly rotates, establishing a constant air flow which removes the heavy vapors from the evaporating surfaces. This method is believed to be one of the most satisfactory of the gravimetric procedures developed to date in that a number of samples may be evaporated simultaneously, and that a simple method of air regulation is employed. For the slower evaporating liquids, however, the time and labor factors are undesirable for routine control work.

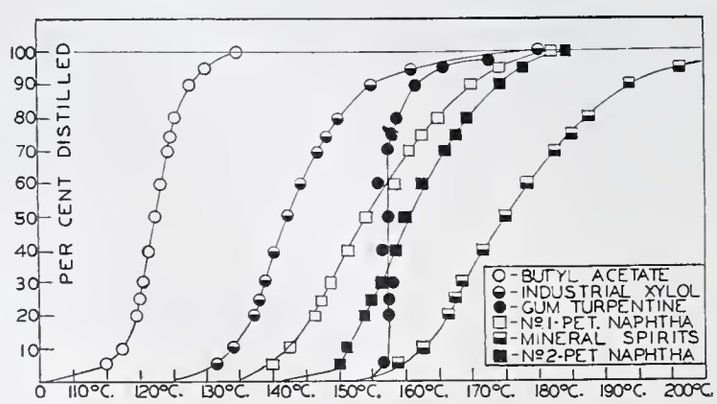

Figure 1. Distillation Curves

At best any method for measuring the rates of evaporation of liquids is not a precise criterion of how these liquids will affect the drying time of finishes. Many factors which affect evaporation rates will affect drying time in different ways. Durrans (*1*) points out that vapor pressure, heat conductivity, latent heat of evaporation, molecular association, surface tension, and humidity are important considerations. He points out further that in mixtures of liquids the molecular attraction of one component by another and the depression of the vapor pressure of one component by another are likewise governing factors. Solvent power and vapor density should be added to the list. A study of the comparative rates of evaporation is therefore of value only in a general sense. In the formulation of a product, selection of likely solvents or thinners can, of course, be made from graphs which express these data, but the materials so chosen must be thoroughly evaluated in the formula in order to establish the one or the blend which most nearly satisfies the properties required. The most specific value to be gained from evaporation data appears to be that of controlling the uniformity of a given liquid as received by the consumer, and of blends which may be prepared prior to manufacture.

With these things in mind the attempt to establish a

rapid, simple, and sufficiently precise method for measuring evaporation rates was approached primarily from the standpoint of control of uniformity. One may rightly inquire why distillation range control should not suffice for this purpose. It is found, however, that samples of a liquid which show good uniformity in this respect do not always show the same uniformity in evaporation characteristics and in fact may even show a reversal of the expected. For example, a recent shipment of a petroleum solvent had a distillation end point of 179° C. and an evaporation end point of 80 minutes. A later shipment had a distillation end point of 185° C. and an evaporation end point of 58 minutes. Both were otherwise essentially the same in distillation percentages. An enamel containing the faster evaporating of these had a "tack-free" time of 4 hours, whereas the slower evaporating solvent caused a 15-minute increase in drying to this stage. It is found also that two liquids having essentially the same distillation dry point may have evaporation end points quite widely separated. No. 1 petroleum naphtha and No. 2 petroleum naphtha shown in Figures 1, 4, and 5 are an outstanding example. A quick-drying enamel dried to the tack-free stage in 3 hours with the faster evaporating of these two solvents as against 3.5 hours with the other.

Further, in connection with distillation-evaporation comparisons among solvents whose chemical composition is distinctly different, distillation curves do not in all cases occur in the same order as evaporation curves even within rather wide limits. The position of gum turpentine with respect to petroleum solvents among the distillation curves in Figure 1, as compared with its position among the evaporation curves in Figures 4 and 5, is illustrative of this point. From the standpoint, therefore, of general usefulness for formulating work as well as control of uniformity, the evaporation data are by far the most desirable.

The apparatus described in this paper and referred to hereafter as the evaporometer is believed to be novel in that its basic principle is volumetric.

Briefly, the assembly of the evaporometer as shown in Figure 2 consists of an air blower, a sulfuric acid wash bottle for drying the air, a manometer, a gas distributor, and graduated sample tubes. The tubes of tapered form are in horizontal position with the sample spread out over maximum area during evaporation, and in vertical position at periodic intervals for volumetric observations. Reasonably good duplication of results is obtained, and the time for each test is short enough for routine control, complete evaporation data being obtained on the average in about one-eighth of the time required for the usual gravimetric procedure. The present apparatus is equipped with three sample tubes, but is limited to this number only by the capacity of the air blower in use.

Rubeck and Dahl (*5*) have shown that for C. P. benzene and petrobenzol variations in humidity normally encountered do not appreciably affect results. Work done by the authors has indicated that this is not true for all solvents and thinners, hence it appears desirable for the present at least to maintain a humidity control.

The evaporometer method is not presented as all-inclusive, since experimental work has been largely confined to liquids having evaporation end points equal to or greater than industrial xylol, eliminating from primary consideration extremely fast-evaporating solvents such as toluene, ethyl alcohol, and 20° benzine. Effort was concentrated on the slower evaporating types, because for them gravimetric methods are time-consuming and difficult to handle in a routine control laboratory. Preliminary work in the range of the fast-evaporating liquids indicates a very appreciable lowering of the temperature during evaporation, causing in some cases a clouding of the liquid which may be due to separation of traces of water. Solvents in this range are being investigated further and the work may culminate in the application of air at an initial temperature above 25° C., since for comparative purposes it is desirable to measure all solvents by the same method. However, should the evaporometer prove to be impractical here, the gravimetric method from the standpoint of rapidity is applicable for control purposes, and it is believed that the Evap-O-Rotor mentioned above should be very satisfactory for these liquids. To put it another way, the evaporometer should be found of greatest interest for the average run of paint and varnish solvents and thinners and the Evap-O-Rotor for lacquer solvents and thinners.

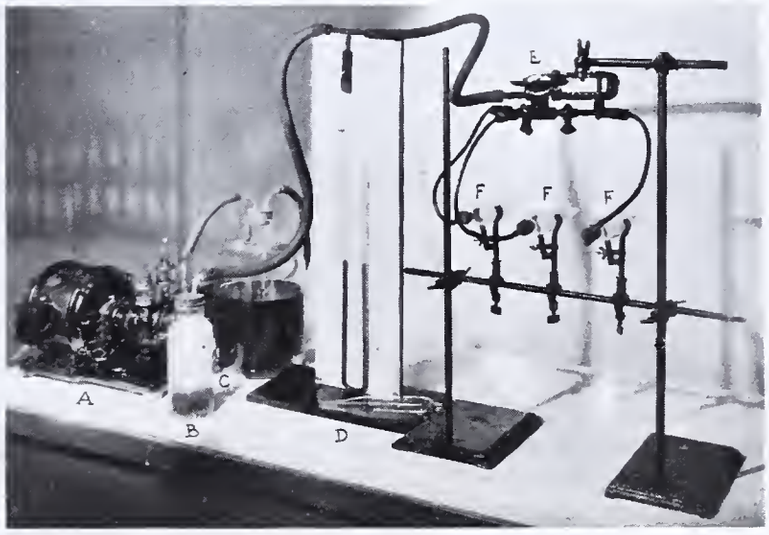

FIGURE 2. EVAPOROMETER

The tubes are in horizontal position for evaporation and are moved to vertical position for volumetric observation.

A. Air blower
B. Trap
C. Drier
D. Manometer
E. Gas distributor
F. Evaporation tubes

Apparatus and Method

The evaporometer assembly is shown in Figure 2.

The air blower is a Boehnke rotary air blast and suction apparatus producing a maximum pressure of 844 grams per sq. cm. (12 pounds per square inch). The acid wash bottle for drying the air is an ordinary 4-liter Pyrex bottle, the lead toward the sample tubes passing through a trap containing glass wool. Beyond the trap is a water manometer. The evaporation tubes are attached to a three-way gas distributor to insure equal distribution of air. The tubes are graduated oil centrifuge tubes with tapered bottom, in accordance with A. S. T. M. specifications for tests D-91-30T and D-96-30. These tubes are made by a number of manufacturers, but the conical dimensions vary among the makers. Those manufactured by the Kimble Glass Company of Vineland, N. J., have been adopted as standard, since they are very uniform and appear to have the clearest glass and the most distinct graduations. No. 1 two-holed rubber stoppers are used with the tubes, one hole carrying the intake and the other functioning as the exhaust. The tubes are held in position by buret clamps which in turn are mounted on a rod suspended between two ring stands. The gas distributor is suspended above the tubes from a universal clamp. The apparatus can be set up as described for about seventy-five dollars.

The evaporometer at present is operated in a constant-temperature room maintained at 25° C. It may be operated outside of a constant-temperature room, however, with good duplication of results either by running a standard each time with samples, or by connecting the air line to a coil immersed in a thermostatically controlled water bath, the latter method supplying air of constant temperature to the sample tubes.

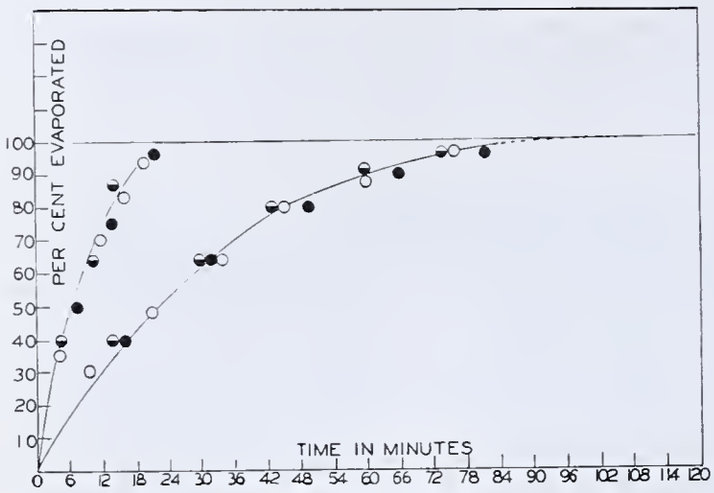

FIGURE 3. REPRODUCIBILITY BY EVAPOROMETER METHOD

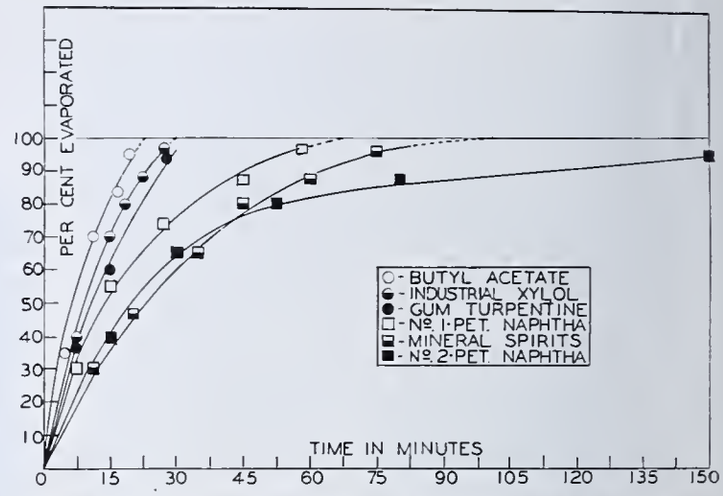

FIGURE 4. EVAPORATION RATES BY EVAPOROMETER METHOD

It is desirable in this case, however, to temper the samples in the tubes before starting the test.

The method of determination requires no special skill or scientific knowledge. Two milliliters of the sample are placed in one of the tubes and the tubes clamped in horizontal position. With the air blower in operation and the manometer adjusted to 20 cm., the stopper is inserted in the tube neck. All tubes are connected during operation whether in use or not, in order to maintain equal air distribution at all times. The exactness of the horizontal position is controlled by observing the point where the area of the surface of the liquid appears perfectly symmetrical.

At intervals, depending upon the speed of evaporation of the solvent under test, the tube is brought to the vertical position and the solvent allowed to drain from the side walls for 1 minute. During this 1-minute period, the meniscus is brought to the level position by slight adjustments of the tube until the maximum bottom curvature of the meniscus is centered in the tube. At the end of the minute, the volume is read with the aid of a magnifying glass, and the tube immediately returned to the horizontal position. All readings are recorded together with the elapsed time. The final reading is taken at approximately the 98 per cent point, since beyond this point the solvent curve does not alter appreciably in slope and can be extrapolated with greater accuracy than can be gained by making further readings. As a matter of convenience, a chart listing the graduations from 0 to 2 ml., together with the percentage corresponding to each graduation, has been prepared for routine use. With normal care, duplication of results to within ±3 per cent from the mean figure of a series of determinations can be obtained on a given sample. Triplicate results on two solvents are shown in Figure 3.

Time-volume graphs of a number of common solvents are shown in Figure 4, and may be compared with the curves obtained gravimetrically, which are shown in Figure 5. The gravimetric data were obtained by evaporating the liquids in 0.5-liter (1-pint) friction-top can covers and making analytical weighings at intervals.

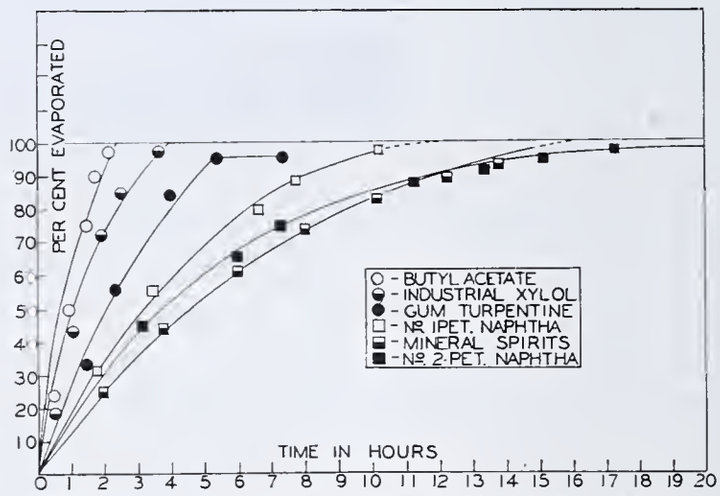

FIGURE 5. EVAPORATION RATES BY USUAL GRAVIMETRIC METHOD

Discussion of Results

It will be noted in Figure 5 that the curve for gum turpentine shows a 3 per cent residue, which is not indicated in the volumetric data in Figure 4. In the volumetric method when the final reading is made this residue does not drain to the bottom during the observation of volume. To determine this residue, in order that the volumetric data may be used, it should be done gravimetrically and the volumetric curve carried to this point. The application of this procedure for liquids containing nonvolatile matter has the advantage over the common gravimetric method in saving of labor, since volumetric observations require but a few minutes and the residue requires but one weighing if the sample is allowed to stand for about an hour beyond the normal evaporating time. The actual labor on solvents of this nature is about one-half of that required for the gravimetric test. On liquids containing no residue the volumetric method reduces labor about two-thirds.

The curves obtained by the two methods, while they are in the same general order, do not exhibit identical proportions of order. This, however, is true of any two gravimetric methods which differ appreciably in mechanical setup or in conditions surrounding the test, such as the rate at which the vapors are removed from the evaporating surface. The latter is believed to be the principal factor involved. In the application of finishes industrially where efficient ventilation systems are used, the vapors are being constantly removed from the surface of the film in a manner more like that in the evaporometer than in any of the gravimetric methods, with the possible exception of those described by Wilson and Worster (*6*) and by Lowell (*4*). Another consideration in this connection is that of all surfaces coated a high percentage are in vertical position during the drying period, and the vapors, being heavier than air, rapidly leave the surface. In the ordinary gravimetric procedure where the vapors remain over the surface of the liquid, a depressing effect on the rate of evaporation is established. Methods, therefore, in which the vapors are constantly removed are believed to be the most practical.

In view of these considerations it appears that the greatest value of the evaporometer lies in the primary consideration which prompted this development—namely, that of reducing the time and labor required for measuring evaporation rates, particularly for the slower evaporating types, with the added

advantage over the usual gravimetric method that the vapors are constantly removed from the evaporating surface.

Summary

Trends in the field of protective coatings emphasize the importance of the evaporation rates of the solvents and thinners used in their manufacture and application. A survey of existing methods reveals that for the slower evaporating types they are time-consuming, lacking in control of air flow, temperature, and humidity, or costly to establish for control purposes. A volumetric method has been described which is rapid, sufficiently precise for control purposes, reasonably inexpensive and which embodies positive control of air flow, temperature, and humidity. The results so obtained, by virtue of the constant removal of vapor from the evaporating surface, are believed to be somewhat more practical than those obtained by methods in which this feature is lacking.

Acknowledgment

The authors are indebted to C. F. Rassweiler and H. H. Hopkins, under whose jurisdiction this work was conducted.

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Determination of Mercury in Iodinated Organic Compounds of Mercury

Application of Spacu and Spacu Copper Sulfate Propylenediamine Reagent

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THE determination of mercury in mercurated organic compounds is of considerable importance, because of the increasing use of such compounds in medicine. Numerous procedures are available, but in the majority of them the halogens and especially iodine are interfering elements and must be gotten rid of. In the potassium thiocyanate titration of mercury, all the halogens must be absent and to accomplish this Kharasch and Flenner (*3*) have developed a very satisfactory method. If iodine is present, mercury cannot be precipitated by Jamieson's reagent, but the procedure of Fenimore and Wagner (*2*) obviates this difficulty. Finally, in the determination of mercury as the sulfide, iodine must be removed by such methods as those of Dunning and Farinholt (*1*) and Tabern and Shelberg (*5*). In three of the above procedures (*2*, *3*, *5*) interfering halogens are eliminated by precipitating the mercury in solution as metallic mercury, which is then redissolved and determined by an appropriate method. Recently Whitmore and Sobatzki (*6*) have developed a new and very direct method for the determination of mercury in organic mercury compounds such as organomercuric halides, by which none of the halogens are interfering elements.

Because of the difficulty mentioned above, it was thought that an adaptation of the method of Spacu and Spacu (*4*) might have possibilities. This paper describes a satisfactory procedure, whereby organic mercury in the presence of iodine is finally determined by the copper sulfate–propylenediamine reagent. The organic mercury compound containing iodine is oxidized in a bomb tube by the well-known Carius method. However, a method of oxidation such as that of Tabern and Shelberg (*5*) should be satisfactory, provided mercuric iodide is not allowed to escape.

The only special reagent required is propylenediamine which is obtainable from the Eastman Kodak Company as a 70 to 75 per cent aqueous solution. The copper sulfate–propylenediamine reagent is prepared by dissolving 2.5 grams of crystalline copper sulfate in water, then adding 2 grams of the propylenediamine solution. It should be made up as needed.

Procedure

Weigh out a sample, corresponding to at least 0.3 gram of mercury, in a small Pyrex weighing tube similar to that used in the Carius halogen determination. To a Carius bomb tube add 3 cc. of fuming nitric acid, transfer the weighing tube carefully to the bomb tube, and proceed as in a halogen determination. After the bomb tube has been heated and cooled (and before opening), heat the capillary end of the bomb tube gently with a gas flame (using goggles), to prevent the loss of any mercuric iodide, which has condensed in that part of the tube, when the capillary is opened. Cut off the end of the tube, add 20 cc. of water and 15 cc. of concentrated ammonium hydroxide, and an amount of solid potassium iodide (plus an excess), sufficient to dissolve the mercuric iodide. Transfer the solution to a 400-cc. beaker and wash out the bomb tube thoroughly with water. Do not allow the total volume to exceed 200 cc. If the solution is brown, owing to free iodine, carefully add clear dilute sodium hydroxide solution until the color is a pale yellow. Heat the solution to boiling and add an excess of hot copper sulfate–propylenediamine reagent. Cool for several hours in an ice-water mixture. Filter the blue precipitate on a weighed Gooch crucible and wash from three to four times with an aqueous solution containing 0.1 per cent of potassium iodide and 0.1 per cent of the copper sulfate–propylenediamine reagent. Then wash three to four times with 2-cc. portions of 96 per cent alcohol and finally two to four times with 2-cc. portions of ether. Dry in a vacuum desiccator and weigh. The precipitate contains 21.81 per cent of mercury.

Considerable preliminary work was carried out to determine whether the method would be satisfactory. A few typical analyses, listed in Table I, are the average of two or more closely agreeing determinations, and indicate the real value of the method. The calculated percentage of mercury is given for compounds I and II which were pure. The remaining compounds were of unknown purity and, for that

TABLE I. TYPICAL ANALYSES

	Calcd. or Known	Found by Spacu and Spacu Method
	%	%
I Mercuric chloride	73.88	73.90
II Tolylmercuric iodide	47.93	47.90
III Chloromercuriphenol	60.66	60.50
IV *p*-Mercury ditolyl	52.07	52.04
V Phenylmercuric chloride	56.14	56.03
VI Phenylmercuric nitrate	62.80	62.87

reason, the mercury content was determined by a sulfide precipitation or by a thiocyanate titration. Compound II was the only one to contain iodine, and therefore, 0.2 to 0.3 gram of diiodofluorescein was added to all the others.

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Microchemical Analysis of Solid Fuels

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THE history of the development of Pregl's methods of quantitative organic microanalysis is familiar to everyone interested in this field. These methods were developed by carrying out analyses on pure organic compounds of known composition. Only after Pregl had demonstrated that his methods were able greatly to reduce the expenditure of time, energy, material, and hence money, and that the results obtained were as accurate and precise as the older macromethods, were the methods accepted by other chemists. Their introduction into industrial laboratories was at first viewed with a good deal of skepticism by industrial chemists, their main argument being that it was impossible for a microsample to be actually representative of the total substance whose analysis was desired.

Certain difficulties are encountered in the elementary macroanalysis of solid fuels, as well as of many other natural substances, such as agricultural and biological products, alkaloids, etc., which are almost entirely absent in dealing with pure organic compounds. In the first place, solid fuels have a complex composition, and all samples, besides containing carbon, hydrogen, and oxygen, also have present nitrogen, sulfur, and mineral matter and sometimes phosphorus and chlorine. Some of these constituents are present in very small amounts, which makes their determination difficult by any method of analysis. In the combustion the mineral matter is converted into ash which may cause certain complications in the analysis. The combustion of solid fuels often leads to the formation of exceedingly combustion-resistant cokes which, at times, makes complete oxidation of the sample extremely difficult. During the expulsion of the volatile matter by the action of heat, large volumes of gas are evolved, consisting primarily of methane, hydrogen, and carbon monoxide, and special precautions must be taken during this part of the combustion to insure their complete oxidation.

Another difficulty involved in the analysis of solid fuels concerns those methods which require solution of the sample. Solid fuels are relatively insoluble and there is no solvent known which dissolves them completely at a moderate temperature and without reaction.

The difficulties connected with the elementary analysis of solid fuels by the usual macromethods have been known for some time and certain modifications of standard methods, as developed on pure compounds, were made by fuel analysts to render the results more certain, consistent, and accurate. In the light of the development of micromethods applied to pure substances, it is now recognized that the conversion of a macro- to a micromethod involves much more than the mere diminution of the size of the sample taken for analysis. Errors which are of no significance in macromethods often assume gigantic proportions in micromethods and much tedious work is necessary for their elimination. It is this rationalization, however, which gives micromethods their accuracy and precision. If such difficulties are encountered in converting macro- to micromethods applied to pure substances, it is only reasonable to expect that the difficulties will be still greater when dealing with complex, heterogeneous substances such as solid fuels.

For the purpose of a systematic discussion, the individual determinations necessary for the complete microanalysis of a solid fuel will be considered.

Sampling Solid Fuels for Microanalysis

Since Pregl, in his development of the methods of quantitative organic microanalysis, was primarily interested in the application of these methods to pure substances, he did not mention in his book the problem of sampling heterogeneous materials for microanalysis. In dealing with pure substances, the microsample taken for analysis is directly a true, diminished representative of the whole. The problem of sampling solid fuels for microanalysis has been fully discussed elsewhere (*25*). In order to obtain homogeneous, representative microsamples, solid fuels must be subjected to extremely fine grinding and thorough mixing.

One difficulty in the fine grinding of solid fuels concerns the extremely troublesome appearance of electrostatic charges induced on the finely ground particles. Great care must be exercised in grinding samples which exhibit this phenomenon, since rather large amounts of the finer particles may be lost from the agate mortar. Various attempts have been made to overcome this difficulty with but moderate success. Such charges can also seriously affect the accurate weighing of microsamples.

Determination of Moisture

The method generally used in this laboratory for determining moisture consists in drying the sample in a microdesiccator at a temperature of 110° to 115° C. for 15 minutes in an atmosphere of nitrogen. The microdesiccator is fitted with a bubble counter which in turn is connected with a Pregl

pressure regulator, both containing concentrated sulfuric acid; the nitrogen is taken directly from a high pressure cylinder. By calibrating the velocity of the bubble rate against the passage of nitrogen, the flow of gas over the sample is known and can never become so violent that particles of the sample are blown out of the boat. In case of hygroscopic samples, all weighings are made in a Pregl stoppered weighing tube.

Vetter (*39*) has devised an apparatus for the direct microdetermination of the moisture content of fuels and other solid substances. The sample is placed in a tube surrounded by a vapor bath—e. g., toluene, b. p. 111° C. A stream of dry nitrogen passes through a pressure regulator and bubble counter, then over the sample, and the moisture is collected in a weighed calcium chloride microabsorption tube, which, in turn, is connected with a Mariotte bottle. By slight modification the apparatus can also be used for vacuum-drying the sample.

Determination of Carbon and Hydrogen

Combustion Tube Filling. The Pregl Universal filling was used by all earlier investigators in determining the applicability of micromethods to coal analysis, and is used in all routine analyses for carbon and hydrogen in this laboratory.

Kopfer (*28*) was the first to point out the advantages of using a platinum-asbestos filling for the combustion of organic substances. For retention of halogens he added a silver spiral and first suggested the use of lead peroxide to retain oxides of nitrogen and sulfur. Haber and Grinberg (*21*) adopted certain of Kopfer's ideas. Their tube filling consisted of a 6-cm. layer of lead chromate held in place by two small copper gauze spirals and a 10-cm. layer of 10–20 per cent platinum-asbestos. The particular advantage of the platinum-asbestos is that the combustion of methane takes place quantitatively at temperatures as low as 410° C., whereas with copper oxide a much higher temperature is necessary, the specifications reaching to a bright red heat and just below the softening point of the hard-glass combustion tube. It was primarily the advantages obtained by this reduction in temperature which led Dennstedt to develop his contact method. The Dennstedt method has also been extended to microsamples, particularly by Funk (*19*) and Friederich (*15*).

There are numerous cases cited in the literature where the elementary analysis of pure substances containing a number of methoxyl or methyl groups has caused considerable difficulty, due to the evolution of methane or carbon monoxide which escape complete combustion, thus yielding low results for carbon and hydrogen. For such difficultly combustible substances, Pregl has used (*22*) and recommended (*31*) a modified Universal filling, removing 6 cm. of the copper oxide–lead chromate portion and substituting for it a 6-cm. platinum star. Pregl, therefore, appeared to favor the presence of a platinum contact in his tube filling when dealing with substances difficult to burn.

If the first portion of the combustion analysis of coal is not conducted carefully, gases, especially methane, may pass through the combustion tube without being burned quantitatively. If the Universal filling is used, the copper oxide–lead chromate layer must be heated to such a high temperature that the tube is likely to be permanently injured after a few combustions, whereas, if only the platinum contact filling is used, great care must be taken to insure an excess of gaseous oxygen always being present.

A tube filled with 40 per cent palladium-asbestos (0.75 gram occupied 15 cm. in an ordinary Supremax microcombustion tube), in place of the copper oxide–lead chromate portion of the Universal filling and using sufficient care during the combustion has been found in this laboratory to yield excellent results for carbon and hydrogen, in the presence or absence of other elements such as halogens, nitrogen, or sulfur (*26*, *27*). Niederl (*34*) has criticized the use of the contact filling. He made calculations of the volume of carbon dioxide and water (steam), which would be formed in the combustion and the volume of oxygen necessary to burn 4 mg. of naphthalene. However, these volume relationships have no significance other than to illustrate the condition which would exist if the entire sample was completely vaporized at a single instant. Naturally, the combustion must be conducted sufficiently slowly so that an excess of oxygen is always present. Dennstedt and also Funk (*19*) insured this condition by having both primary and secondary oxygen inlets, while Friederich (*16*) used a countercurrent pyrolysis of the sample in order to achieve a stepwise combustion of the sample. In this laboratory the sample was merely vaporized very slowly and regularly. From the typical analyses cited by Friederich and Funk it is apparent that the contact filling is capable of yielding satisfactory results in the microdetermination of carbon and hydrogen.

The use of the palladium-asbestos contact filling in this laboratory also yields satisfactory results. This is indicated by the results in Table I, obtained on fairly large samples of naphthalene. The samples were dried over phosphorus pentoxide, drawn into capillaries while molten, sealed, and weighed. The analyses were made on a hot, humid, August day.

Table I. Analyses on Naphthalene

Weight of Sample	Found C	Found H	Difference from Theory C	Difference from Theory H
Mg.	%	%	%	%
6.385	93.48	6.28	−0.22	−0.02
7.916	93.59	6.40	−0.11	+0.10
8.638	93.55	6.38	−0.15	+0.08
7.102	93.69	6.35	−0.01	+0.05

It would appear that a compromise between the Universal and contact filling, as used by Pregl and Haber, would be a logical way in which to avoid the disadvantages of each. With such a filling the platinum contact will easily effect the oxidation of methane and there still will be an oxygen "reservoir" present, in the form of the copper oxide–lead chromate, to oxidize any incompletely oxidized decomposition products which might persist due to an insufficient amount of gaseous oxygen to complete the oxidation. This modified tube filling is therefore suggested for the carbon-hydrogen determination in fuels or for compounds which are known to evolve methane during combustion.

Absorption Tube Fillings. In the Coal Research Laboratory only Ascarite is used for the absorption of carbon dioxide. It has been found that the finer mesh (20 to 30) material is extremely well suited for microanalytical purposes. Having a much larger surface for a given weight than the 4- to 8-mesh material, many more analyses can be made without the necessity of refilling the tube. Thus, a 3.5- to 4.0-cm. layer in a 7- to 8-mm. outside diameter absorption tube absorbed over 400 mg. of carbon dioxide from 21 analyses made on various fuel samples weighing from 6 to 10 mg. before the tube filling was exhausted to a point where further use might have entailed loss. No cases of stoppage have so far been encountered.

For absorption of water either Dehydrite (magnesium perchlorate trihydrate) is used, or phosphorus pentoxide deposited on pumice, as recommended by Boëtius (*4*). Dehydrite should never be placed in direct contact with cotton, as suggested by Pregl when using calcium chloride. Any mineral acid which might reach the desiccant could react, forming perchloric acid, which in turn could explosively oxidize the cotton or any other organic material present. A layer of glass wool is used to separate either of the above drying agents from the small layer of cotton placed in the end of the absorption tube. When absorption tubes filled with phosphorus pentoxide–pumice are used, the tubes are weighed filled with oxygen, the capillaries being stoppered with tight-fitting pins, also as suggested by Boëtius.

The advantages of using oxygen only in microdeterminations of carbon and hydrogen in industrial laboratories are discussed by Vetter (*38*), who points out that air, free of or-

ganic and absorbable inorganic vapors, is not likely to exist in the vicinity of an industrial plant in which the microchemical laboratory is located. This air, if used, contains sufficient harmful materials to influence the accuracy of the carbon-hydrogen determination. He recommends using oxygen only and weighs the absorption tubes filled with oxygen, unstoppered. A concomitant advantage is that the combustion requires less time, since the final sweeping can be done with 50 cc. of oxygen, a complete carbon-hydrogen determination requiring but 40 minutes.

Determination of Ash

The determination of ash is generally made in connection with the carbon-hydrogen or sulfur determination, the boat merely being weighed after combustion. Precautions must be taken during the combustion so that no ash is lost due to spattering. In burning dry samples this is most likely to occur during the time the volatile matter of the fuel is being actively evolved.

In independent ash analyses the Pregl micromuffle is used. A useful modification of this apparatus has been suggested by Coombs (*9*). The disadvantages of the rather crude Pregl apparatus are pointed out and in place of the bent tube it is suggested that a straight silica tube be used which can be fitted with a bubble counter and pressure regulator, so that the velocity of the air, or where necessary, oxygen, which passes over the sample can be accurately regulated. The use of oxygen in the determination of ash in solid fuels is a great advantage, as combustion with air is a very slow process, particularly when dealing with coke, anthracite, or graphite.

Determination of Nitrogen

The Kjeldahl or Dumas method is generally used for the determination of nitrogen in solid fuels. There appears to be a considerable difference of opinion among fuel analysts as to which method gives the most reliable results. Pregl developed microprocedures for both these methods, being primarily interested, however, in their application to pure organic compounds. In both the macro- and micromethods certain difficulties are encountered in the analysis of solid fuels if they are used in their "standard" form. Other methods for determination of nitrogen in solid fuels have been suggested, but to date have not been developed on microsamples.

The Kjeldahl Method. As pointed out by Terres (*37*), Kjeldahl published his method in 1883 and applied it to the determination of nitrogen in natural substances such as cereals. The advantages of the method in simplicity, convenience, economy of time, and adaptability to series analyses caused it to be immediately recognized and it was rapidly adopted for general analytical practice and used in the analysis of all types of substances. After a few years a great deal of experience was gained and numerous modifications, such as those of Wilfarth, Gunning, Arnold, and others, were made in order to speed up the method still further. It is now well known that certain types of nitrogen linkages in organic compounds prevent the successful use of the Kjeldahl method, but with a knowledge of the structure of the substance being analyzed, one can predict with a good deal of certainty whether or not the method or one of its modifications can be expected to yield quantitative results. However, very little is known regarding the type of nitrogen linkage in solid fuels, so that it would be impossible to predict whether or not the Kjeldahl method could be expected to yield quantitative results.

Bunte and Schilling (*6*) applied the Kjeldahl method to the analysis of solid fuels shortly after it was published and found it yielded very consistent results. The method was retained for fuel analyses, largely on the basis of Bunte's results, and even at present it is the method mainly used for routine nitrogen determinations on solid fuels. The question as to whether this method actually determines the total nitrogen in solid fuels was really never further tested until 1919, when Terres made an exhaustive study of the problem. As a result of his investigation, Terres concluded that the "standard" Kjeldahl method (he actually used the Kjeldahl-Gunning method, adding potassium sulfate to the concentrated sulfuric acid), applied to solid fuels, always gave low results. The amount of nitrogen found in the sample was a function of the manner in which the digestion was carried out; the highest values were obtained when the digestion was done at relatively low temperatures—that is, with prolonged low-temperature digestion. The values obtained by the Kjeldahl and Dumas methods (the latter including a subsequent combustion with oxygen) may differ by as much as 46 per cent for coal and 32 per cent for coke. These facts are indicated in Table II.

Table II. Effect of Digestion Temperature on Kjeldahl Determination of Nitrogen in Various Fuels

	Temperature, ° C.					Diff. (Dumas and Kjeldahl)	
	250	275	300	325	Dumas[a]	High	Low
Peat, % nitrogen	1.70	1.56	1.46	1.36	1.72	− 1.2	−20.4
Hours digested	221	50	14	3	..	....	....
Brown coal, % nitrogen	0.80	0.76	0.62	0.58	1.08	−25.9	−46.3
Hours digested	282	77	35	4.5	..	....	....
Saar coal, % nitrogen	1.31	1.23	1.15	1.00	1.73	−24.4	−42.1
Hours digested	408	118	44	4.5	..	....	....
Ruhr coal, % nitrogen	1.33	1.26	1.20	1.07	1.55	−14.2	−31.0
Hours digested	491	142	74	6	..	....	....
Anthracite, % nitrogen	1.35	1.34	1.24	1.13	1.72	−21.5	−34.3
Hours digested	623	213	59	15.5	..	....	....
Peat coke, % nitrogen	..	0.82	0.73	0.71	0.89	− 7.9	−20.2
Hours digested	..	50	22	12	..	....	....
Brown coke, % nitrogen	..	0.55	0.52	0.44	0.62	−11.3	−29.0
Hours digested	..	96	69	28	..	....	....
Saar coke, % nitrogen	..	1.11	1.01	0.98	1.43	−22.4	−31.5
Hours digested	..	117	63	48	..	....	....
Ruhr coke, % nitrogen	..	1.53	1.48	1.34	1.59	− 3.8	−15.7
Hours digested	..	45	24	18	..	....	....
Anthracite coke, % nitrogen	..	1.49	1.27	1.22	1.79	−16.8	−31.9
Hours digested	..	48	30	24	..	....	....

[a] Subsequent combustion in oxygen.

As a result of this work Terres maintained that, in order to get correct results by this method, the gases evolved during digestion must be collected and analyzed for their elementary nitrogen content since a considerable portion (as much as 50 per cent) of the total nitrogen present may be evolved in this form and so is not converted into ammonia. This is shown in Table III.

Table III. Proportionation of Nitrogen in Kjeldhal Determination on Solid Fuels

	Nitrogen			N_2/NH_3	
Fuel	As NH_3 %	As N_2 %	Total %		Dumas[a] %
Peat	1.32	0.42	1.74	24	1.72
	1.36	0.43	1.79	24	
Brown coal	0.57	0.61	1.18	52	1.08
	0.64	0.58	1.22	48	
Saar coal	1.33	0.42	1.75	24	1.73
	1.13	0.65	1.78	37	
Ruhr coal	1.19	0.46	1.65	28	1.55
	1.09	0.42	1.51	28	
Anthracite	1.20	0.62	1.82	34	1.72
	1.14	0.72	1.86	39	

[a] Subsequent combustion in oxygen.

This work of Terres casts grave suspicion on the use of the "standard" Kjeldahl method for the determination of nitrogen in solid fuels. His results have recently been confirmed by Börnstein and Petrick (*5*).

According to Carlile (*7*), the elementary nitrogen found by Börnstein and Petrick may have come from air which was incompletely removed from the apparatus, from occluded and adsorbed nitrogen in the coal and in the reagents used, or from cumulative traces of air in the carbon dioxide used to sweep the apparatus. According to Carlile's results, the Kjeldahl-Wilfarth-Gunning method is adequate for the nitrogen determination in solid fuels. Also, Fieldner and Taylor (*11*) and Baranov and Mott (*2*) claim that if the Kjeldahl-Wilfarth-Gunning method (use of sulfuric acid, potassium sulfate, and mercury or mercuric oxide in digestion) is applied to solid fuels, satisfactory results are obtained which agree with modified Dumas determinations. Beet (*3*) added selenium to the above list of catalysts used during digestion and claimed to obtain more rapid, but still satisfactory, results.

If considerable quantities of elementary nitrogen are lost during the macrodigestion of solid fuels, it is very probable that similar losses will occur during microdigestion. Micro-Kjeldahl determinations on coal and coke samples made in the Coal Research Laboratory have yielded practically identical results to those obtained by other laboratories using the macro-Kjeldahl method on the same samples. If an error is present in the macromethod it is also present to approximately the same extent in the micromethod. This whole question of validity can be settled satisfactorily only by further careful research on the two methods.

In this laboratory the ammonia, on distillation, is absorbed directly in boric acid solution and titrated with standard acid using methyl orange as indicator, as first suggested by Winkler (*42*) for the macrodetermination and applied to the microdetermination by Allen (*1*), Stover and Sandin (*36*), and Meeker and Wagner (*32*). The advantage of this procedure is that but one standard solution is necessary.

THE DUMAS METHOD. The Dumas method is also not free of suspicion when applied to the analysis of solid fuels, nor even when applied to certain pure nitrogen-containing compounds. It frequently yields high results on substances containing a large number of methyl groups, presumably because of the formation of methane or carbon monoxide, which escape complete oxidation in the presence of copper oxide in an atmosphere of carbon dioxide, and hence are measured along with the nitrogen. Still other substances form combustion-resistant cokes under these conditions, making it very difficult or impossible to obtain complete combustion in an atmosphere of carbon dioxide, even when intimately mixed with fine copper oxide, low results then being obtained. Incomplete combustion can, therefore, lead to high or low results, depending upon whether the combustion of the coke or the gaseous thermal decomposition products is incomplete.

Terres (*37*) made a careful study of the Dumas method applied to solid fuels and found that complete combustion of the fuel could be obtained only provided a subsequent oxidation was conducted using gaseous oxygen. However, it is again very important to make an exact analysis of the resulting gas collected in the azotometer, since only about one-third of this gas is nitrogen. The method is definitely complicated by this procedure, but Terres claims that only with this modification of the Dumas method can accurate and reliable results be obtained for the nitrogen content of solid fuels. This has been confirmed by a number of investigators (*10, 13, 18, 23, 30*).

The difficulties mentioned in connection with the macro-Dumas method are also involved in the micromethod. In his book, Pregl stated that occasionally one meets a substance, which on heating with copper oxide in an atmosphere of carbon dioxide forms a nearly incombustible, nitrogen-containing coke. In such cases he recommended that the sample be mixed with potassium chlorate and fine copper oxide. It has since been pointed out, however, that such a procedure is purposeless, since the potassium chlorate is completely decomposed and has furnished all of its oxygen (at 350° to 400° C.) long before the portion of the tube containing the sample is strongly heated and even before the combustion-resistant coke is actually formed. Lead chromate or potassium dichromate is probably better suited for this purpose since they evolve oxygen only when heated to high temperatures. According to Friederich (*14*), none of these subterfuges solve the difficulty, the nitrogen values only being raised by a few tenths of a per cent. If larger amounts of oxidizing agents are used, higher values for nitrogen are obtained but duplicate analyses often vary by several per cent. Addition of these materials to compounds which yield satisfactory results with copper oxide alone also give results which are too high, owing to the passage of either excess oxygen or carbon monoxide into the azotometer.

TABLE IV. COMPARATIVE DETERMINATIONS

	Micro-Dumas	Kjeldahl Micro	Kjeldahl Macro	Micro-Dumas / Micro-Kjeldahl
	%	%	%	%
Coal A	0.48	1.21	1.24	40
Coke A	0.14	0.86	0.86	16
Edenborn coal	1.61	1.52	1.60	105.9

Fleischer (*12*) also pointed out that the micro-Dumas method, developed on pure compounds, cannot be applied to coal and coke without modification of the method and the apparatus, because these substances have a very low nitrogen content and are difficult to burn, all of the nitrogen escaping only after complete combustion of the sample. From 2 to 4 mg. of a coal sample containing 1 per cent of nitrogen only 0.016 to 0.032 cc. of gas will be obtained. These amounts are too small for accurate measurement even by the micro-azotometer. Fleischer, therefore, recommends a somewhat larger apparatus than that used by Pregl and burns samples weighing from 50 to 100 mg. mixed with about 20 grams of lead chromate so that from 0.3 to 1.00 cc. of nitrogen are obtained. This amounts essentially to a semi-micromethod. Terres also included the micro-Dumas method in his above-mentioned investigation. He used samples weighing about 35 mg. and carried out a subsequent combustion of the residual coke with gaseous oxygen. He found that the subsequent oxidation yielded only insignificant amounts of nitrogen and the final values obtained were considerably lower than even the values obtained by the Kjeldahl method.

In the experience of the Coal Research Laboratory the micro-Dumas and Kjeldahl methods yield practically identical values for nitrogen when applied to Edenborn coal (the coal being intensively investigated in this laboratory), while other coals yield values by the micro-Dumas method which are very much lower than either the micro- or macro-Kjeldahl values. This is illustrated in Table IV; the micro-analyses were made by F. C. Silbert. If a weighed amount of potassium chlorate was mixed with the copper oxide and sample, larger amounts of nitrogen were obtained, but if the amount of gas collected in a blank determination with the same weight of potassium chlorate was deducted, the increase in nitrogen was insignificant. It was also found that if the fine copper oxide, containing the residue from the Dumas combustion, was removed and digested with sulfuric acid as in a micro-Kjeldahl determination, an appreciable amount of ammonia was obtained on distillation with alkali.

Vetter (*40*) has devised what might be called an ultra-microazotometer for use in micro-Dumas determinations on substances with very low nitrogen content, such as solid and liquid fuels. The azotometer is made of 1-mm. capillary so that a length of 1 mm. contains but 0.8 cu. mm.; 1 mm. in Pregl's azotometer contains about 10 cu. mm. However, if

the combustion of the sample is incomplete, it is futile to refine the azotometer to this extent.

The microdetermination of nitrogen in solid fuels, using existing procedures, is inadequate and should be modified to meet the very special requirements imposed upon it by these substances. Work is now under way in this laboratory on this problem. The aim of this investigation is to develop a method which will result in complete, visual combustion of the sample and yield only pure nitrogen as the gas collected in the azotometer.

Determination of Sulfur

The main difficulty encountered in the microdetermination of sulfur in solid fuels, whether by the combustion or the Carius method, is due to the low sulfur content of these materials. These methods are conducted under such conditions that complete visual destruction of the sample is insured and no difficulty is met regarding incomplete oxidation. However, using Pregl's standard procedures, these methods will not yield the same value for sulfur on most solid fuels, since the micro-Carius method determines the total sulfur of the sample and the microcombustion method determines only the volatile sulfur. Fortunately, Edenborn coal has a negligible amount of nonvolatile sulfur, so that the microcombustion method yields essentially the same values as the macro-Eschka method.

The micro-Carius method is not convenient for routine series analyses and Merten (*33*) of the I. G. Farbenindustrie Laboratory modified Pregl's microcombustion method so as to determine the total sulfur in solid fuels. Fifty- to 150-mg. samples are weighed into a large platinum boat and mixed with twice their weight of Eschka mixture. The combustion is conducted in oxygen and oxides of sulfur are absorbed in perhydrol present on the beads or the spiral in the combustion tube. The boat and its contents are removed and boiled with water and the perhydrol solution from the combustion tube is also added, the solution filtered, acidified, and the barium sulfate precipitated as usual.

The filtration of minute amounts of barium sulfate through the micro-Neubauer crucible is a rather inconvenient procedure, even with the Wintersteiner modification, and in this laboratory the filter stick and crucible devised by Emich are now used exclusively. Guillemet (*20*) recommends the use of the benzidine-hydrochloride method for the microdetermination of sulfur in substances of low sulfur content. The sulfuric acid resulting from the combustion of the sample is precipitated as benzidine sulfate and collected and weighed in a Jena fritted-glass filter. The filtration is said to be more rapid and simple than with barium sulfate.

An investigation is now under way in this laboratory to develop a rapid, volumetric method for determination of total or volatile sulfur in solid fuels. The presence of nitrogen in the sample is a complicating factor, since nitrogen-containing acids are formed during the oxidation and must be eliminated before an acidimetric titration can be made. Friederich and Watzlaweck (*17*) have developed a microvolumetric method for just such cases, but the procedure is somewhat complicated for routine purposes.

Determination of Methoxyl

In the determination of the methoxyl content of various derivatives obtained from coal in this laboratory, the microvolumetric method of Vieböck and Brecher (*41*) is exclusively used. This method has been found to be extremely rapid and very well suited to series analyses. A possible difficulty has been pointed out by Kuhn and Roth (*29*) in connection with the methylimide group determination, and might also affect the methoxyl determination. They found that in dealing with certain substances, low results were often obtained which were traced to the insolubility of the samples in the reagents used in the determination. Methylated derivatives of fuel products, such as humic acids, or other high molecular weight compounds, are also insoluble in most organic solvents and a similar difficulty may be encountered here. In the absence of a standard for comparison it is difficult to know whether or not correct analytical results are obtained on such samples. The volumetric method, however, yields good checks on duplicate determinations and also agrees with the results obtained by the semi-microvolumetric method of Clark (*8*).

Determination of Molecular Weight

None of the methods described by Pregl appear suitable for the microdetermination of the molecular weight of solid fuels or of high molecular weight products derived from them. The Pregl ebullioscopic method is unsatisfactory for these substances, first, because of their insolubility in most solvents, and, second, because the change in boiling point caused by these high molecular weight substances is extremely small and, because of frequent and large fluctuations in the atmospheric pressure in Pittsburgh, is difficult to determine accurately. The micro-Rast method is also unsuitable for these substances because they form such deeply colored melts with camphor and other, more recently discovered, cryoscopic solvents possessing high constants, that it is practically impossible to determine the melting point depression. Solubility is also low in these solvents.

The semi-microcryoscopic method, developed by Smith and Howard (*35*) in the Coal Research Laboratory for use with complex fuel products, utilizes catechol or biphenyl as the solvent. Catechol is the best solvent known at present for substances of this type. A microcryoscopic method has been described by Iwamoto (*24*), using the Pregl-Beckmann thermometer. Pure samples were used weighing 7 to 30 mg. and with molecular weights of 180 to 480, quite accurate results being obtained. Using catechol as solvent, this method could probably be adapted for use with solid fuels and their products.

Direct Determination of Oxygen

The apparatus developed in this laboratory for the direct microdetermination of oxygen in solid fuels (*26*) is essentially a modification of Pregl's apparatus for the microdetermination of carbon and hydrogen. The most important features of the modification consist of the Sprengel pump for circulating oxygen over the sample during combustion, and the thermostating of the entire apparatus for the purpose of getting constant temperatures from which to calculate the volume of oxygen consumed during the combustion. The principle of the method consists in burning the sample in a closed system of known volume, filled with oxygen, and determining the weight of the combustion products and the weight of the oxygen consumed during the combustion. The oxygen in the sample is then equal to the difference between the sum of the weight of the oxygen content of the combustion products and the weight of oxygen consumed. The method was developed on pure compounds, starting first with substances containing only carbon, hydrogen, and oxygen, then adding halogens, nitrogen, and finally sulfur; then, after the various details had been worked out, the method was applied to solid fuels (*27*).

The presence of halogens in the compounds caused no difficulties. In the case of sulfur compounds (*27*), the data indicate that the sulfur is completely oxidized to sulfur trioxide under the specific conditions used in this work. In the case of nitrogen-containing substances (*27*), knowledge of the

fate of the nitrogen after combustion was necessary. The hypothesis is advanced that the form in which the nitrogen appears after combustion is a function of the manner in which it is linked in the compound. It is suggested that, under the specific conditions of the combustion method used, all nitrogen compounds yield their nitrogen as nitric oxide and nitrogen, the ratio of these products, in case of amines and amides, being different from that obtained from nitriles, nitro-, and nitrogen-heterocyclic compounds.

Experiments are now being carried out in order to get further evidence in support of this hypothesis as well as to get some definite information as to the mechanism by which lead peroxide absorbs oxides of nitrogen which are formed during the combustion of nitrogen-containing compounds.

Summary

The difficulties involved in the application of Pregl's micromethods to the analysis of solid fuels are pointed out and the advantages of certain modifications, at present in use, are discussed. These modifications are necessitated by the unique physical and chemical characteristics of solid fuels which involve (1) their complex composition, (2) the low percentage of several of the constituents present, (3) the possibility of incomplete combustion of gaseous decomposition products, (4) the formation of highly combustion-resistant cokes, (5) their limited solubility in all solvents, and (6) the lack of a definite standard to which analytical results can be compared. Still other modifications to existing methods are suggested, some of which are in process of investigation in the Coal Research Laboratory.

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Titration of Fluorine in Biological Materials

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FLUORINE can be isolated from inorganic samples by distillation as hydrofluosilicic acid (*3*), and titrated in the distillate with cerium nitrate (*1*) in the presence of a mixed indicator (*2*). In organic materials, the problem is somewhat complicated by the necessity of ashing the samples without losing fluorine, and of obtaining the ash in such condition that the subsequent isolation and titration of the fluorine will not be interfered with.

Fluorine in organic substances has been titrated before; a variety of elaborate and unreliable methods have been used and the results have always been inconsistent. As there are only minute amounts of fluorine in plant or animal tissues, the details of the chemical procedures become all-important. Therefore, standardized conditions for calcination, distillation, and titration are now presented, not on a basis of new principles but as simple and correct procedures which combine the desirable features of the various methods selected.

Preparation of the Samples

The tissues obtained after necropsy are cleaned, washed, weighed, placed in individual containers, and kept in a refrigerator until ready for analysis. They are transferred to silica dishes, the containers are washed with hot water, the washings are transferred to the dish, and in the case of small samples, such as the heart, lungs, spleen, and kidneys, 50 to 100 cc. of a saturated solution of lime are added. To the large samples 2 to 15 grams of finely powdered calcium oxide are added, the amount depending on the size of the sample; to bones or teeth, no lime is added; to the liver of a guinea pig, 0.5 gram of lime is added; this is needed to prevent fusion on ashing, as well as loss of fluorine by volatilization. The samples are dried by keeping the dishes for several days on an electric heater at medium heat. The major part of fat-containing samples is burned by inserting a wick and igniting while on the hot plate.

The dried samples are burned out in an electric muffle furnace at 600° C. Teeth and bones require a higher temperature, 650° to 700° C. Liver samples fuse readily, unless a fairly large amount of lime has been added. Other samples do not fuse at

600° C., but in silica dishes may lose fluorine at a higher temperature. The burning out is completed after 12 to 24 hours, except in the case of teeth, which require 48 hours at 650° to 700° C. After grinding in a mortar and weighing, the samples are ready for analysis. The large samples, such as bones, muscle, and remainders, are weighed before grinding. The actual weight of the ash is determined by subtracting the weight of the lime added from the total weight. The ratio of the actual ash weight to the total weight is used to calculate the amount of fluorine per gram of ash after determining the fluorine in the calcined sample. Ash samples weighing less than 1.5 grams are used in their entirety.

The long drying of the sample was necessary to avoid splattering and loss of the sample when it was placed in the muffle furnace. It was also found that samples containing unoxidized carbon were difficult to distill and gave low results; consequently the ignition was carried out as completely as possible at these temperatures.

Isolation of the Fluorine

The ash is decomposed with perchloric acid and the fluorine is distilled off as hydrofluosilicic acid (*3*). The distillation apparatus consists of a 25-cc. round-bottomed flask with a neck 10 cm. in length. A side arm is attached 4 cm. from the top of the neck, and is bent in an inverted U-shape to prevent contamination of the distillate by bumping. More elaborate trapping devices are inadvisable, because adsorption causes fluorine deficiencies. The side arm is connected by a ground joint to a small vertical condenser which delivers the distillate into a 125-cc. Erlenmeyer flask. The neck of the distilling flask carries a rubber stopper (which should be replaced after three operations), fitted with a thermometer and the capillary stem (2 to 3 mm.) of a dropping funnel. Both the thermometer and capillary extend to within 5 mm. of the flask bottom. The flask is mounted over the 2-cm. hole of an asbestos pad and is heated by a microburner. Fastened by small clamps to a single ringstand, this device makes a fairly compact unit.

An accurately weighed sample of ash (1.0 to 1.5 grams) is placed in the flask, with 3 cc. of water and several small pieces of silicon carbide. The rubber stopper, condenser, and receiver are attached. Enough water is placed in the receiver to permit a 5-mm. immersion of the condenser tip during the first 5 minutes of the distillation. Five cubic centimeters of 60 per cent perchloric acid are fed through the funnel. The heating is started and when the liquid temperature reaches 135° C., 50 to 75 cc. of water are slowly dropped from the funnel to compensate for the water distilling out, and to maintain the temperature at 135° C. (Small triangular grooves cut on opposite sides of the stopcock of the dropping funnel improve the regulation of the water flow and hence the constancy of the temperature.) For small amounts of fluorine, 50 cc. should be distilled; for larger amounts, 75 cc. are needed. The distillation requires constant supervision and takes from 45 to 90 minutes. It is inadvisable to allow the temperature to rise above 140° C.

Titration of the Fluorine

The condenser is detached and washed with a jet of water, which is added to the distillate. Several drops of 0.04 per cent phenol red solution are added, and the liquid is neutralized with dilute sodium hydroxide, avoiding a large excess. The alkaline solution is boiled and repeatedly brought back to the apparent neutral point with 0.02 *N* or 0.01 *N* perchloric acid. During this neutralization, the volume is reduced to 5 to 10 cc. When the faint pink color is no longer restored by boiling (carbonate-free), the solution is cooled, transferred quantitatively to a 50-cc. beaker, and boiled from about 25 cc. down to 2 to 3 cc. Two drops of saturated alcoholic solution of methyl red and 10 drops of 0.04 per cent bromocresol green solution are added. (The bromocresol green is weighed out exactly and neutralized with standard sodium hydroxide to yield the monosodium salt. This prevents alteration of the neutrality of the solution when the indicator is added.) The liquor is titrated at 80° C. to the maximum red color with cerous nitrate solution (1 cc. ≈ 0.5 mg. of fluorine). When the amount of fluorine is less than 0.2 mg., thorium nitrate solution (1 cc. ≈ 0.1 mg. of fluorine) may be substituted for the cerous nitrate, using the same mixed indicator.

Results

Calcium fluoride was prepared and analyzed with the results shown in Table I.

Table I. Analysis of Precipitated Calcium Fluoride

Fluorine found, mg.	3.54	2.80	2.44
Fluorine calculated, mg.	3.46	2.87	2.48

The correction for blanks using thorium nitrate was established by the titration of sodium fluoride solutions without distillation, as shown in Table II, and consequently a uniform 0.02-mg. correction was adopted.

Table II. Establishment of a Blank Correction

Present, mg.	0.070	0.050	0.040	0.040	0.032	0.030	0.022	0.020	0.015	0.010	0.009	0.000	0.000
Found, mg.	0.072	0.070	0.050	0.058	0.042	0.036	0.050	0.034	0.032	0.034	0.026	0.022	0.020
Difference	0.002	0.020	0.010	0.018	0.010	0.006	0.028	0.014	0.017	0.024	0.017	0.022	0.020

The method itself was tested by dividing the samples, measuring the fluorine content of one part, adding a known amount of calcium fluoride to the other, measuring its fluorine content, and comparing the analytical results with computed data. The results appear in Table III. The ashed samples used weighed from 1.0 to 1.5 grams.

Table III. Analysis of Ashed Samples with Added Fluorine

	Found in Ash	Added as CaF_2	Total Calcd.	Total Found
	Mg.	*Mg.*	*Mg.*	*Mg.*
Blood	0.55	3.43	3.98	3.99
Bone	0.12	3.65	3.77	3.70
	0.29	4.72	5.01	4.93
Liver	0.27	3.23	3.50	3.58
Muscle	0.14	5.01	5.15	5.12
	0.14	4.77	4.91	4.90
	0.24	2.97	3.21	3.16
Oats	0.10	1.22	1.32	1.30
	0.10	2.97	3.07	2.92
Teeth	0.14	1.12	1.26	1.26
	0.15	0.92	1.07	1.14
	0.40	0.78	1.18	1.17
	0.40	0.78	1.18	1.03

Discussion

The titration proposed by Willard and Winter, using small amounts of fluorine, was unsatisfactory in the authors' hands. The above method gives a sharp end point and the results on solutions of known fluorine content (0.03 to 5.0 mg.) could be duplicated with only small errors.

The fluorine content of the lime used (Merck's reagent quality) was too slight to affect the titration appreciably. The amount of lime in any of the ashed samples used was never over 40 per cent of the total weight. Analysis of 10 grams of the lime gave a fluorine concentration of 0.0019 per cent.

Summary

A standard procedure has been given for ashing plant and animal tissues for the volatilization of the fluorine present by distillation with perchloric acid and for the titration of this fluorine with cerous nitrate or thorium nitrate. Amounts of fluorine as low as 0.02 mg. may be determined.

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Volumetric Determination of Iron in Leather

Wet Oxidation of Organic Matter Using Mixed Nitric, Perchloric, and Sulfuric Acids and Titration of Iron, Using Titanous Chloride

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THE wet oxidation of the organic matter in chrome-tanned leather by a mixture of nitric, perchloric, and sulfuric acids has been shown (*5*) to be rapid and quantitative. Following the destruction of organic matter, the chromium is oxidized to chromic acid by the excess of perchloric acid and is then determined, using an excess of ferrous sulfate, with back-titration using ceric sulfate or potassium permanganate with ortho-phenanthroline ferrous complex as indicator. The presence of more than traces of iron in vegetable-tanned leathers is claimed to be detrimental. The wet oxidation of the organic matter in finished leathers following the previously cited method, if adaptable to the case of 5- to 10-gram samples, might make the volumetric determination of small amounts of iron possible by direct titration, using a standard solution of titanous chloride with ammonium thiocyanate as internal indicator. The determination of iron in finished chrome-tanned leather by the same process would also be possible. After reduction of the chromic acid by boiling with dilute hydrochloric to form chromic ion, if the green color thus produced does not mask the color of the thiocyanate end point, the process would be suitable.

The purpose of this paper is to describe conditions under which iron can be determined rapidly and quantitatively, in both vegetable- and chrome-tanned leather following wet oxidation, using standard titanous chloride. The influence of the chromic ion by color interference in this titration has been determined through a study of the potentiometric evaluation of the end point of the reaction. A series of finished leathers has been analyzed by the process, both in the presence and absence of chromium, and the accuracy of the process proved by the adulteration of prepared sample solutions of oxidized leather residues with known amounts of iron. Interest is added to this investigation by the attempt now being made to adapt iron salts as substitutes for chromium salts in the tanning of leather. (Iron salts for tanning have been used particularly in Russia and Germany, and are reported in their present state of development to give an inferior leather product. Iron, if present in amounts much in excess of a few hundredths of 1 per cent in vegetable-tanned leather, seems to have a detrimental effect due to ill-defined causes, *2*.)

Previous Investigations

Small amounts of iron in tanning extracts are generally determined colorimetrically by the thiocyanate method. Merrill and Henrich (*3*) determine the iron in finished leathers by ashing the sample, with gravimetric determination of iron in the solution of the ash, using ammonium hydroxide. The separation of aluminum from the iron was made by means of sodium hydroxide. Bergman and Mecke (*1*) use an indirect method for the determination of iron following the determination of chromium in chrome-tanned leather. Their method leaves much to be desired, since ferrous sulfate was used in the titration of the chromium and the total iron thus present was determined and the iron used in the chromium reduction subtracted. This procedure is of interest in comparison with the present process, since perchloric acid was used in the wet oxidation of the leather sample. By the present process, employing nitric and sulfuric acids to which perchloric acid is added, the wet oxidation requires much less time and higher temperatures may be employed.

Reagents and Standard Solutions

LEATHER OXIDANT. Two volumes of 70 to 72 per cent pure perchloric acid (sp. gr. 1.67) mixed with one volume of 80 per cent analytical reagent sulfuric acid (sp. gr. 1.73).

NITRIC ACID. Analytical reagent grade (sp. gr. 1.42).

AMMONIUM THIOCYANATE. A 10 per cent solution free from iron was prepared.

POTASSIUM FERRICYANIDE. As ordinarily purchased from stock, this reagent is of high purity. It is prepared for use by being ground to a fine powder and dried at 135° to 140° C. for 1 hour or longer.

TITANOUS CHLORIDE. Stock solutions in hydrochloric acid of approximately 20 per cent strength may be purchased. The technically pure grade supplied by the Vanadium Corporation of America was found to be very satisfactory. Iron, if present, had no undesirable influence following the operations subsequently to be described. Sufficient amounts of this solution to give an approximately 0.01 *N* solution were dissolved in a given volume of dilute (1 to 20) hydrochloric acid and stored under hydrogen using a Zintl and Rienäcker (*6*) automatic buret.

STANDARDIZATION OF TITANOUS CHLORIDE. Accurately weigh individual 100-mg. samples of dry powdered potassium ferricyanide and transfer to the 500-ml. reaction flask shown in Figure 1. The side opening of the flask is closed during the digestion of the sample for the decomposition of the ferricyanide. Add 10 ml. of leather oxidant. Close the reaction flask with the refluxing digestion head shown in Figure 1 and digest just below the boiling point. The solution blackens from the formation of colloidal carbon. The carbon is soon oxidized, leaving the solution almost colorless. When the reaction is complete a slight yellow color from free chlorine finally remains after a 15- to 30-minute digestion. A precipitate of anhydrous ferric sulfate is formed.

Cool somewhat, dilute with 20 to 30 ml. of water, and remove the refluxing digestion head, washing it inside and outside with a stream from the jet of the wash bottle. Boil the solution 2 to 3 minutes to remove chlorine and dissolve the dehydrated ferric sulfate. Dilute the solution to 100 ml. with ice water and replace the side stopper of the flask with the gas bubbler tube (Figure 1). Add 10 ml. of ammonium thiocyanate solution and flush out the air using a brisk stream of carbon dioxide gas with the titration head shown in Figure 1 in place. Continue the passage of a brisk stream of carbon dioxide and titrate with the solution of titanous chloride to be standardized. The reaction between ferric sulfate and titanous chloride is slow and the last few drops are added at half-minute intervals. The color change from deep red to pink to colorless is sharp and can be determined within one drop of 0.01 *N* titanous chloride. Duplicate titrations are averaged, from which data the standard value of the solution is calculated using 329.19, the theoretical value for the equivalent weight of $K_3Fe(CN)_6$. The process as described is essentially the same as that of Smith and Getz (*4*), except that leather oxidant is used for simplicity in this case and improved apparatus of greater convenience is employed.

The stability of titanous chloride stored as described by Smith and Getz (*4*) was shown by repeated titration after long continued use. The data are given in Table I.

Table I. Stability of Approximately 0.01 *N* Titanous Chloride Stored under Hydrogen

(Reference Standard $K_3Fe(CN)_6$)

Time, days	7	20	53	67
Normality	0.01424	0.01425	0.01421	0.01411

Table II. Leather Samples Analyzed

Leather No.	Trade Name	Type	Cr_2O_3 Content %	Sample Form
1	Korry-Krome	Chrome	3.57	Chips
2	Stadri No. 1	Chrome	3.73	Chips
3	Not specified	Chrome	3.50	Ground
4	Stadri No. 2	Chrome	3.73	Ground
5	Logger's Oak	Vegetable-tanned	..	Chips
6	Duxbak	Vegetable and chrome	..	Chips
7	Tioga Oak	Vegetable-tanned	..	Chips
8	L and M	Vegetable-tanned	..	Chips
9	Armour's Joppa	Vegetable-tanned	..	Chips

Preparation of Samples

Nine samples of leather were used for test analyses. Four were chrome-tanned, four were vegetable-tanned, and one sample was tanned by the combined vegetable- and chrome-tanning process. The descriptions of these samples are given in Table II.

Attempts to prepare samples of vegetable-tanned leathers for analysis by use of a revolving-knife shreading mill always met with failure. Samples thus prepared were never uniform in iron content and errors of 100 per cent or more in the determined amount of iron, which is ordinarily present to the extent of 0.01 to 0.02 per cent in vegetable-tanned leathers, are not uncommon. This was proved beyond doubt by comparison analyses of vegetable-tanned leathers after shreading and in the form of chips: In the former case analyses were always high and in poor concordance; in the latter case duplicate analyses were always in agreement and much lower in value by comparison. In the case of chrome-tanned leathers the "loading agents," paraffins and waxes, prevent the abrasive effect on the knife blades of the shreading mill. The samples of leather in most cases were cut into chips the thickness of the leather and approximately 1 mm. in width by 3 to 4 mm. in length.

Titration of Ferric Iron

Effect of Green Chromic Ion. For the determination of iron in chrome-tanned leather, the influence of the green chromic ion upon the disappearance of the ferric thiocyanate color, after complete reduction by titanous ion, might be predicted to involve the development of a premature end point. Since the amounts of chromium in finished chrome leathers are within narrow limits the same, approximately 3.5 per cent Cr_2O_3, for a given weight of sample the amount of chromium present is fairly constant.

To learn the extent to which this premature end point affects the determination of iron, a series of analyses of a standard solution of ferric perchlorate by titration with approximately 0.01 *N* titanous chloride was made in the presence of increasing amounts of chromic ion. For this study a standard solution of ferric perchlorate (25.00 ml. equivalent to 18.15 ml. of 0.01424 *N* titanous chloride) was added to 10 ml. of leather oxidant and evaporated to fumes of perchloric acid. The solutions thus obtained were adulterated by addition of known amounts of potassium chromate diluted, hydrochloric acid was added, and the chromium reduced by boiling. The samples thus obtained were cooled by dilution and titrated with titanous chloride after the addition of ammonium thiocyanate using a stream of carbon dioxide in the titration apparatus shown in Figure 1.

The results of these analyses are shown graphically in Figure 2. The amounts of Cr_2O_3 in milligrams added are plotted on the horizontal axis and the corrections in terms of milliliters of 0.01424 *N* titanous chloride are plotted on the vertical axis. The end point, as in all subsequent determinations, was determined by transmitted light from a

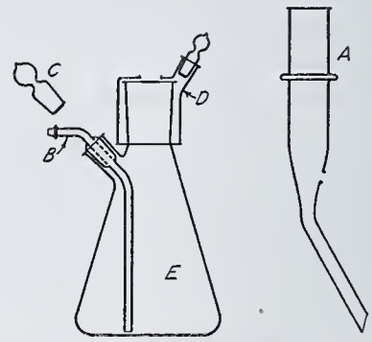

Figure 1. Digestion and Titration Apparatus

daylight lamp bulb against a white background. The color change at the end point is a change from an intense red color of the ferric thiocyanate through an olive or yellowish green, finally to a clear light green with no tint of olive green. The last few drops of standard solution should be added with half-minute intervals between additions.

An examination of Figure 2 will show that the magnitude of the end-point error is directly proportional to the increase in amount of chromic ion present. The correction for the use of a 5-gram sample of chrome-tanned leather is approximately 0.2 ml. of 0.01 *N* titanous chloride (185 mg. of Cr_2O_3). The correction in the case of vegetable-tanned leather is 0.05 ml. of 0.01 *N* titanous chloride, since in such case 10 to 15 mg. of chromic oxide were added during the destruction of the organic matter to indicate the completion of the reaction. The correction is to be added in each case, since the end point appears prematurely.

The magnitude of the end-point error was further studied, using the potentiometric method. With a calomel half-cell and platinum wire reference electrode system and low hydrogen-ion concentration the magnitude of the end-point deflection was found to be approximately 200 mv. with 0.05

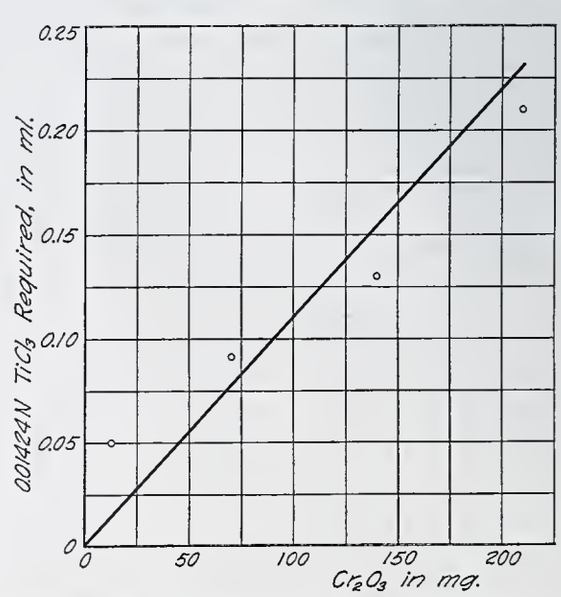

Figure 2. Influence of Chromic Ion on Thiocyanate End Point

ml. of 0.01424 N titanous chloride. Conditions for these determinations duplicated essentially the experimental procedure given above for the visual end-point determination and the correction there found was substantiated. The visual end-point correction has been further tested by the separation of the iron in digested leather samples from the chromium, followed by volumetric determination.

Oxidation of Organic Matter and Preparation of Solutions

Procedure for Chrome-Tanned Leather. Weigh 5 grams of finished leather in the form of chips or shreads and place in a 500-ml. digestion flask (Figure 1) with the stopper adjusted in the side arm. Add 25 ml. of leather oxidant and 10 to 15 ml. of concentrated nitric acid. Digest at a moderate temperature (125° to 150° C.) on an electric hot plate or substitute device capable of satisfactory temperature control and with the refluxing digestion head in place, allow the reaction of oxidation to progress 15 to 30 minutes or until the mixture begins to blacken from deposited carbon. Add 10 ml. more of concentrated nitric acid and continue the digestion an additional 15 to 20 minutes, gradually raising the temperature to approximately 200° C. The excess nitric acid is completely volatilized at this point and fumes of perchloric acid appear in the flask. As soon as the last traces of organic matter are oxidized by the hot perchloric acid, the green solution turns orange because of oxidation of chromium to chromic acid. The decomposition of the last traces of organic matter and the oxidation of chromium are exothermal reactions and copious fumes of perchloric acid appear at this point.

Cool somewhat, wash and remove the refluxing digestion head, and add 50 ml. of 1 to 1 hydrochloric acid. Boil gently for 10 minutes to reduce chromic acid, evolve chlorine, and decompose possible traces of nitric acid which would react with titanous chloride. Cool and dilute by the addition of 150 ml. of cold water. Replace the flask stopper with the gas bubbler tube, place the titration head (Figure 1) in position, and bubble a brisk stream of carbon dioxide through the reaction mixture. Titrate with 0.01 N titanous chloride (after the addition of 25 ml. of 10 per cent ammonium thiocyanate) until the red color begins to fade. Add the titrating liquid dropwise until the pink tinge fades to olive green. The final few drops of titanous chloride should be added at half-minute intervals until by transmitted light the solution turns clear green with no tinge of olive or yellowish green. Using an artificial light source against a white background, the end point is detected within one to two drops of titrating liquid. Add 0.2 ml. to the titer found, to correct for the premature end point due to the presence of the green chromic ion. The results of a series of analyses of chrome-tanned leather are given in Table III.

Table III. Determination of Iron in Chrome-Tanned Leather by Titration with Titanous Chloride

Leather No.	Leather Grams	0.0142 N $TiCl_3$ Ml.	Fe_2O_3 Found Gram	Fe_2O_3 Found %
1	5.053	1.30	0.0015	0.029
	5.379	1.58	0.0018	0.033
	5.624	1.52	0.0017	0.031
			Av.	0.031
2	5.089	4.60	0.0052	0.103
	5.163	4.90	0.0056	0.108
	5.019	4.74	0.0054	0.107
			Av.	0.106
3	4.819	5.10	0.0058	0.120
	5.526	5.84	0.0066	0.120
	5.446	5.46	0.0061	0.114
			Av.	0.118
4	5.915	8.66	0.0098	0.166
	5.393	7.40	0.0086	0.160
	5.890	8.30	0.0097	0.164
			Av.	0.163

The analyses of the four samples of leather in Table III were repeated and known quantities of iron (0.0041 mg. calculated as Fe_2O_3) added as ferric perchlorate solution, using a transfer pipet for the additions. The adulterated samples had been previously prepared just as for the analyses of Table III and the ferric perchlorate solution added before the destruction of organic matter was completed. The data obtained are contained in Table IV.

Table IV. Determination of Iron in Chrome-Tanned Leather after Adulteration with Additional Iron Titration with Titanous Chloride

Iron added as $Fe(ClO_4)_3$ solution equivalent in each case to 0.0041 gram of Fe_2O_3

Leather No.	Leather Grams	0.0142 N $TiCl_3$ Required Ml.	Fe_2O_3 Found Gram	Fe_2O_3 Calcd. Gram	Error Fe_2O_3 Mg.	Fe_2O_3 in Leather %
1	5.023	4.96	0.0056	0.0057	−0.1	0.032
	3.396	4.34	0.0049	0 0052	−0.3	0.024
	5.092	4.62	0.0053	0.0057	−0.4	0.024
				Av.	−0.3	0.027
2	5.024	8.34	0.0095	0.0091	+0.4	0.108
	5.014	7.80	0.0089	0.0091	−0.2	0.096
				Av.	+0.1	0.102
3	5.709	9.80	0.0111	0.0108	+0.3	0.123
	5.612	9.24	0.0105	0.0106	−0.1	0.114
	5.526	9.24	0.0105	0.0106	−0.1	0.116
				Av.	±0.0	0.118
4	5.251	11.30	0.0128	0.0126	+0.2	0.166
	5.786	11.24	0.0128	0.0135	−0.7	0.150
	5.171	11.00	0.0125	0.0125	±0.0	0.162
				Av.	−0.2	0.159

The values given for the calculated amounts of Fe_2O_3 shown in column 4 of Table IV are based upon the analyses of each leather sample shown in Table III, to which calculated Fe_2O_3 present in the leather, the amount of Fe_2O_3 added in the form of ferric perchlorate, has been added. The values in column 5 are obtained from the same figures. The values in column 6 were obtained on the assumption that the added iron had been correctly determined. The values in column 6, Table IV, are therefore to be compared with the values of column 5, Table V. The agreement in the Fe_2O_3 content of the various samples is found to be satisfactory.

As a further check of the accuracy of the analyses, particularly the error, if any, involved in the end-point correction as applied in Tables III and IV, the same samples were digested as before to decompose organic matter and oxidize the chromium. The iron was then precipitated, together with any aluminum present, by ammonium hydroxide, filtered, washed, and dissolved in hot, dilute hydrochloric acid. The solutions thus obtained were titrated with titanous chloride exactly as previously described but in the absence of chromium. The values thus obtained required no end-point correction and are given in Table V.

Table V. Determination of Fe_2O_3 in Chrome-Tanned Leather by Titration of Ferric Iron

Using titanous chloride after separation of iron from chromium

Leather No.	Leather Grams	0.0142 N $TiCl_3$ Required Ml.	Fe_2O_3 Found Gram	Fe_2O_3 Found %	Average Per Cent Fe_2O_3 in Leather: Cr absent	Cr present	Fe_2O_3 added
1	5.019	1.42	0.0016	0.032			
	5.067	1.40	0.0016	0.031	0.032	0.031	0.027
2	5.016	4.44	0.0051	0.101			
	5.054	4.36	0.0050	0.098	0.100	0.106	0.102
3	5.284	5.50	0.0063	0.118			
	5.665	5.70	0.0065	0.114	0.116	0.118	0.118
4	6.040	8.60	0.0098	0.162			
	6.072	8.60	0.0098	0.161	0.162	0.163	0.159

The values in the last two columns of Table V are taken from the results of Tables III and IV, respectively, and on the whole are satisfactorily comparable with them. The accuracy of the end-point correction found according to the data of Figure 2 as applied in Tables III and IV is thus proved.

Finally, additional samples of the same chrome-tanned leather were digested and prepared for titration with titanous chloride. The end point of the titration was determined first visually using ammonium thiocyanate and with the same solutions potentiometrically, since the end point in the latter case always appears after the visual end point. The values obtained are shown in Table VI.

Table VI. Comparison of Visual and Potentiometric End Points

Leather No.	Leather Grams	0.0142 N $TiCl_3$: Visual Ml.	Potentiometric Ml.	Difference Ml.	Fe_2O_3 Found: Visual %	Potentiometric %
1	5.009	1.30	1.50	+0.20	0.029	0.034
2	5.257	4.34	4.50	+0.20	0.094	0.097
3	4.578	4.92	5.04	+0.12	0.112	0.118
4	6.283	9.00	9.20	+0.20	0.161	0.165

By examination of the data of Table VI it will be observed that the magnitude of the end-point error formerly determined—namely, 0.20 ml. of 0.0142 N titanous chloride—is substantiated.

Preparation for Determining Iron in Vegetable-Tanned Leather

The preparation of finished vegetable-tanned leather for titration of iron using titanous chloride differs somewhat from the preparation of finished chrome-tanned leathers. The "loading agents," such as paraffin, waxes, and other fillers, used in the case of chrome-tanned leathers are absent. The absence of these fillers causes the leather to be more readily and vigorously oxidized if the same procedure is employed as that previously described. This fact makes it advisable to pretreat the leather sample, using concentrated nitric acid alone to be followed by the addition of leather oxidant ($HClO_4 + H_2SO_4$). The iron present in finished vegetable-tanned leather varies from 0.01 to 0.03 per cent, which requires larger samples of leather for analysis. Even with suitable 6- to 8-gram samples of vegetable-tanned leathers (because of the absence of loading agents) as compared to 5-gram samples of chrome-tanned leather, the volume of leather oxidant required is less. The absence of chromium is beneficial, since the amount of iron present is low. The more vigorous nature of the attack by nitric acid requires that samples of vegetable-tanned leather be digested with greater care and hence somewhat greater time intervals are required for the destruction of organic matter. The complete destruction of organic matter is readily indicated if 20 to 25 mg. of potassium dichromate are added to the sample during the digestion. The chromium is reduced to chromic ion in the presence of organic matter and after its complete destruction is at once oxidized to chromic acid, from the orange color of which the digestion of the sample is known to be complete.

Procedure for Vegetable-Tanned Leather. The same apparatus and method of heating as that previously described for chrome-tanned leather are employed, using 8- to 10-gram samples.

Add 10 to 15 ml. of concentrated nitric acid plus 25 mg. of potassium chromate and heat if necessary until the evolution of oxides of nitrogen diminishes materially. Add 15 ml. of leather oxidant and digest at gradually increasing temperatures until the nitric acid is completely evolved and the fumes of perchloric acid appear after a temperature of approximately 200° C. is attained and the last traces of organic matter are destroyed and the orange color of chromic acid appears. If excessive charring occurs before the final oxidation stage is reached, add 5 to 10 ml. of concentrated nitric acid before heating to the last stage of the reaction. The remainder of the analysis is conducted exactly as described in the case of chrome-tanned leather.

Test analyses of five leathers were carried out following the procedure as outlined. Check analyses of the same leathers were made either by the process of addition of known amounts of iron or by first separating the iron as ferric hydroxide. The results of these analyses are shown in Table VII. A correction for premature thiocyanate end point of 0.05 ml. of 0.0142 N titanous chloride was applied in each case.

Table VII shows that in all cases, with the possible exception of sample 8, the analyses are satisfactorily consistent and closely duplicated by direct and modified procedures. Amounts of iron of the order of 1 to 2 mg. are determinable with an accuracy of ±0.1 to 0.2 mg. or less.

The summarization of all results is given in Table VIII. The second column gives the determination of Fe_2O_3, in presence of the chromium of the sample or the small amount added, by the recommended procedure. The third column gives the iron determination in cases in which iron was added to study the accuracy of recovery of the original iron present. The fourth column shows the determination of iron in case of its prior separation as ferric hydroxide. In Table VIII the values are to be compared in the horizontal rows, and are found in comparatively excellent agreement.

Table VII. Determination of Iron in Vegetable-Tanned Leathers by Titration with Titanous Chloride

Leather No.	Grams	Fe_2O_3 Added Gram	0.0142 N $TiCl_3$ Ml.	Fe_2O_3 Found Gram	Fe_2O_3 Found %	Fe_2O_3 Calcd. Gram	Error Mg.	Method of Checking Analysis
5	8.267	....	0.63	0.0007	0.009	....	...	.....
	7.903	....	0.65	0.0007	0.009	....	...	.....
	7.992	0.0041	4.33	0.0049	0.010	0.0048	+0.1	Iron added
	8.256	0.0041	4.41	0.0050	0.011	0.0048	+0.2	Iron added
				Av.	0.010			
6	5.223	....	1.20	0.0014	0.026	....	...	.....
	5.655	....	1.10	0.0013	0.022	....	...	.....
	5.423	....	1.10	0.0013	0.023	....	...	.....
				Av.	0.024			
7	6.575	....	0.86	0.0010	0.015	....	...	Iron pptd.
	7.448	....	1.15	0.0013	0.018	....	...	.....
				Av.	0.017			
8	8.096	....	2.05	0.0023	0.029	....	...	.....
	7.205	....	1.35	0.0015	0.021	....	...	.....
	7.513	....	2.05	0.0023	0.031	....	...	.....
	7.445	....	1.20	0.0014	0.018	....	...	Iron pptd.
				Av.	0.025			
9	8.782	....	1.55	0.0018	0.020	....	...	.....
	8.962	....	1.95	0.0022	0.025	....	...	.....
	4.652	0.0041	4.41	0.0050	0.019	0.0052	−0.2	Iron added
	9.072	....	1.32	0.0015	0.017	....	...	Iron pptd.
				Av.	0.020			

Table VIII. Summarized Results of Determinations of Fe_2O_3 in Chrome- and Vegetable-Tanned Leathers

Leather No.	Fe_2O_3 Direct Titration: Cr present or added %	Fe_2O_3 Direct Titration: Cr present and Fe added %	Fe_2O_3 after Pptn. of $Fe(OH)_3$ %
1	0.031	0.027	0.032
2	0.106	0.102	0.100
3	0.118	0.118	0.116
4	0.163	0.159	0.162
5	0.009	0.011	...
6	0.024	...	...
7	0.018	...	0.015
8	0.027	...	0.018
9	0.023	0.019	0.017

Possible Hazardous Reactions

There are no hazardous reactions involved in the wet oxidation of the organic matter in leather following the process herein described. It should be noted, however, that the reactions of digestion, if pushed too vigorously through the use of too great application of heat, may result in the samples' catching fire in the digestion flask. This need not result if some experience in carrying out the digestion is acquired. No explosions were obtained throughout the hundreds of digestions employed in connection with this work, and in no case was the use of a screen between operator and digestion equipment deemed necessary. After the nitric acid oxidation is complete in the case of chrome-tanned leather the solutions boil gently and quietly until the perchloric acid concentrates to approximately 70 per cent strength, when a vigorous exothermal reaction takes place. For vegetable-tanned leathers the reaction temperature is lowered and the applied heat is checked if the reaction progresses too briskly. With vegetable-tanned leathers using 25 ml. of nitric acid no charring results even with 8- to 10-gram samples.

Summary

1. A method involving the wet oxidation of organic matter in finished chrome- and vegetable-tanned leathers, including filler material such as oils, greases, and paraffins, has been developed.

2. Separations are unnecessary, as hexavalent chromium is reduced by boiling with hydrochloric acid, and the iron may then be determined by direct reduction with standard titanous chloride solution, and ammonium thiocyanate as indicator.

If desired, iron may first be separated from hexavalent chromium by precipitation with ammonia and then determined with titanous chloride.

3. Fifty-seven determinations of nine different leathers, both chrome- and vegetable-tanned, show that the new method is accurate within ±0.01 per cent of the Fe_2O_3 present in the case of chrome-tanned leathers, and within ±10 per cent of the iron present in vegetable-tanned leathers for 0.01 to 0.03 per cent total Fe_2O_3 content.

4. Hazardous reactions following the new method were not encountered and the speed of analysis by comparison with existing methods is improved without sacrificing accuracy.

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Loss of Water-Soluble Potash in Fertilizer Mixtures

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THE fertilizer materials that are used as sources of nitrogen and phosphoric acid may be divided into two classes according as they are soluble or insoluble in water. Those that are soluble in water are recognized to be available to plants, and methods based on treatments other than water-extraction have been adopted for determining the availability of those that are water-insoluble. Since all the potash materials used are readily water-soluble, they too have been recognized as available. A method based on the extraction of the sample with water was therefore adopted for determining the availability of potash in all types of mixed fertilizers, and with slight modifications has been used in this country during the past 50 years.

The claim has frequently been made, however, that extraction with water does not recover all the soluble potash incorporated in mixed fertilizers and that any method based on water-extraction does not give a true measure of the availability of the potash in fertilizer mixtures. This view was first suggested by Carpenter in 1901 in a report to Hare (*13*), referee on potash for the Association of Official Agricultural Chemists. Experimental data in support of this view have been presented by different investigators (*4, 5, 6, 11, 18, 19, 20*) and various modifications of the method for determining potash availability have been suggested (*4, 5, 6, 11*).

The failure to recover all the soluble potash included in a fertilizer mixture has been explained on the assumptions that a portion of the potash is fixed by siliceous or other constituents of the superphosphate with which it is mixed (*2, 4, 5, 6, 18, 20*); and that the loss is apparent rather than real because of errors in the analytical procedure following extraction (*3, 4, 10, 16, 18, 21*).

In a recent investigation of the subject, Thornton and Kraybill (*23*) found that the residues obtained after leaching mixed fertilizers with water as directed in the official method for determining potash availability, all contained considerable amounts of potash and that this residual potash is available to plants as determined both by the Neubauer method and by pot tests.

The present paper gives the results of a study of the problem that was undertaken at the suggestion of the Chemical Control Committee of the National Fertilizer Association. The work was limited to an investigation of the cause of the loss of water-soluble potash in fertilizer mixtures and of the extent to which this loss takes place.

Experimental

Consideration of the problem suggested that loss of potash might occur (1) by reaction with constituents of the mixture to precipitate a water-insoluble compound, (2) by occlusion within caked particles of the mixture, (3) by base-exchange reaction with siliceous or claylike constituents in the superphosphate component of the mixture, and (4) by adsorption by the gel-like or amorphous ingredients of the mixture.

Insoluble Potash Salts. The best known of the more insoluble potash salts are syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$, potassium fluosilicate, K_2SiF_6, potassium fluoaluminate, K_3AlF_6, and potassium metaphosphate, KPO_3.

When pure syngenite is brought into contact with water at 100° C. decomposition takes place with deposition of gypsum until the solution contains 1.05 per cent of potassium sulfate (*14*). The potash in this material would therefore be expected to be entirely available as determined by the official method and this was found to be true both in tests made with the c. p. product and with a sample of material supplied by the U. S. Bureau of Mines. The latter sample was obtained as a by-product in the extraction of potash from polyhalite.

Potassium fluosilicate has a solubility of 0.546 gram per 100 grams of water at 100° C. (*7*). When a 2.5-gram sample was washed as described in the official method it was found that about 55 per cent remained undissolved. The potash in this material is therefore not completely available as determined by the official method. The maximum quantity of potassium fluosilicate that could be present in a 2.5-gram sample of a mixed fertilizer if all the fluorine in the mixture were combined in this way would not exceed 0.1 gram. This quantity will dissolve completely when washed with 200 cc. of hot water, as shown by tests with the c. p. product and with a sample of impure material supplied by the International Agricultural Corporation. The impure material was collected as a crystalline product in the bottom of phosphoric acid storage tanks.

Potassium fluoaluminate has a solubility of only 0.158 gram per 100 grams of water (*8*). It requires an alkaline medium for its preparation and could therefore not be formed in the ordinary fertilizer mixture.

Potassium metaphosphate that is formed by double decomposition is entirely water-soluble as determined by the official method but the ignited product is only partially water-soluble when slowly cooled. There is no possibility, however, that the latter would be formed in fertilizer mixtures of the ordinary type.

No evidence has thus been obtained to indicate that there is any loss of potash as a result of the formation of any of the compounds listed, but this does not preclude the possibility that loss of potash may occur by precipitation in the form of some unknown compound.

Table I. Analysis of Citrate-Insoluble Residues

Material	Residue in Percentage of Original Material	Composition of Residues							
		Loss on ignition at 1000° C.	K_2O	CaO	P_2O_5	Fe_2O_3	Al_2O_3	SiO_2	F
		%	%	%	%	%	%	%	%
Ammoniated Florida pebble superphosphate	12.9	6.3	0.06	27.1	18.5	1.60	0.19	43.9	3.10
Tennessee superphosphate	9.8	4.6	0.08	19.9	13.0	0.83	0.24	59.3	2.85
Florida pebble superphosphate	1.6[a]	23.3	0.24	11.6	4.3	2.30	0.50	47.4	0.72

[a] Most finely divided portion of residue which amounted to 6.7 per cent of the original material.

Occlusion in Caked Particles. In studying the possible loss of potash by occlusion in caked particles, quantities of potassium chloride and potassium sulfate were mixed with separate portions of plaster of Paris and sufficient water was added to hydrate the entire mass. The hard cakes obtained on standing for a month were crushed to pass a 20-mesh screen and 2.5-gram samples of the screened materials were washed with 200 cc. of boiling water. The residues were analyzed for potash but none was found.

In a second experiment one part of potassium chloride was mixed with 5 parts of Florida pebble superphosphate. A corresponding mixture was also prepared with potassium sulfate. The mixtures were then moistened with water, dried to induce caking, and the caked mass in each case was crushed to pass a 20-mesh screen. Portions of each of the resulting products (2.5 grams) were then washed with boiling water as in the preceding test, and potash was determined in the residue by the J. Lawrence Smith method. No greater amount of potash was found, however, than in the residues from similar superphosphate–potash salt mixtures that had not been dried so as to induce caking.

Base Exchange Reaction. It is known that potash is absorbed by the colloidal silicates in the soil and that the potash occurring in a combination of this kind cannot all be recovered by the degree of washing specified in the official method for water-soluble potash. It is also well known that phosphate rock matrix contains soil colloids or claylike constituents. In washing the rock an attempt is made to remove as much of these constituents as possible but it is impractical to remove them entirely, and there is therefore the possibility that constituents of this kind may be contained in superphosphate made from the rock. A study was accordingly undertaken of the extent to which the water-soluble potash in a fertilizer mixture may be retained by base-exchange reaction with the siliceous or claylike constituents of the superphosphate present. In making these tests, 1000 grams of each of three superphosphate samples were washed with water and then digested with neutral ammonium citrate solution as directed in the official method for determining citrate-insoluble P_2O_5. The purpose of this treatment was to concentrate the clay constituents of the superphosphate as much as possible without destroying their base-exchange capacity. The citrate-insoluble residues obtained were washed and dried. The compositions of the residues are given in Table I.

The analysis of the residues shows that the combined iron oxide and alumina content does not exceed 3 per cent in any case. The sesquioxides in a soil colloid usually range between 25 and 45 per cent (*22*). It is improbable that the sesquioxides in the residues are present entirely as soil colloidal material, but if this is assumed to be the case the soil colloids in any of the residues should not exceed 12 per cent, or 1 per cent on the basis of the original superphosphate. The quantity of potash that a soil colloid will adsorb varies greatly with different colloids, but the maximum that any soil colloid will retain after washing is not likely to exceed 2 per cent. It may be concluded therefore that the maximum amount of potash that any of the superphosphates used in the tests can retain by base exchange will not exceed 0.02 per cent, or 0.10 per cent on the basis of the P_2O_5 in the superphosphate.

A weighed portion of each of the residues was allowed to stand in a 10 per cent potassium chloride solution for 3 days, washed with boiling water as directed in the official method, and analyzed for potash by the J. Lawrence Smith method. The potash found was the same as before treatment with the potassium chloride solution. The tests indicate that any base-exchange capacity which phosphate rock may possess is destroyed in the process of converting it into superphosphate.

Adsorption in Amorphous Ingredients. It has long been known that amorphous compounds will remove more or less soluble salts from the solution in which they are precipitated. Gordon (*12*) has shown, for example, that when alumina and ferric oxide gels are treated with a 0.1 *N* potassium sulfate solution the former will take up 1.1 per cent of its weight of potash from the solution and the latter 0.5 per cent.

The removal of electrolytes from solution by colloids of this nature may take place both by occlusion and adsorption. Amorphous materials may form a protective coating over materials with which they are associated and the removal by washing of soluble salts occluded in this way may be difficult. The mechanism of adsorption of electrolytes by colloids is not clearly understood, but it is known that the degree of adsorption may vary with the concentration, acidity, and nature of the electrolyte and that an element may be removed from solution in the ionic form or in molecular combination.

Superphosphate contains such amorphous ingredients as silicic acid, organic matter, and various simple and complex combinations of iron and aluminum. Of these amorphous ingredients the phosphates of iron and aluminum are present in much the largest proportions. With a view to determining the capacity of these materials for retaining potash, quantities of each were prepared by treating solutions of ferric chloride and of aluminum chloride with equimolecular proportions of monoammonium phosphate, the solutions were made alkaline with ammonia, and the precipitates that formed were filtered off and washed. Known quantities of the potash-free products prepared in this way were treated with potassium chloride in various ways. The treated samples were then leached with boiling water (*1*) and potash was determined in the residues. It was found, as shown in Table II, that when dry iron or aluminum phosphate was soaked for one day in a 10 per cent potassium chloride solution, filtered, and washed, more or less potash always remained in the residue. The

quantity retained in this way was increased when moist freshly precipitated iron or aluminum phosphate was substituted for the dry product, or when the phosphates were precipitated in a 10 per cent potassium chloride solution.

TABLE II. RETENTION OF POTASH BY IRON AND ALUMINUM PHOSPHATES

Phosphate	Treatment	Potash Retained in Percentage of Phosphate	Potash Retained in Percentage of P_2O_5 in phosphate
Ferric phosphate, dry	Soaked in 10 per cent KCl solution for 1 day and washed	0.73	2.26
Aluminum phosphate, dry	Soaked in 10 per cent KCl solution for 1 day and washed	0.15	0.37
Ferric phosphate, moist, freshly precipitated	Soaked in 10 per cent KCl solution for 1 day and washed	3.41	7.19
Aluminum phosphate, moist, freshly precipitated	Soaked in 10 per cent KCl solution for 1 day and washed	3.73	6.44
Ferric phosphate	Precipitated in a 10 per cent KCl solution containing $FeCl_3$ and $NH_4H_2PO_4$ by adding NH_3	1.01	2.15
Aluminum phosphate	Precipitated in a 10 per cent KCl solution containing $AlCl_3$ and $NH_4H_2PO_4$ by adding NH_3	1.44	2.49

TABLE III. VARIATION IN LOSS OF WATER-SOLUBLE POTASH IN CURED SUPERPHOSPHATE–POTASH SALT MIXTURES WITH IRON AND ALUMINUM CONTENT OF SUPERPHOSPHATE

(K_2O/P_2O_5 in mixture = 1 to 2)

Phosphate No.	Superphosphate	Composition of Superphosphate K_2O %	Fe_2O_3 %	Al_2O_3 %	P_2O_5 %	Total Potash Rendered Insoluble by Superphosphate in Mixture with: KCl %	K_2SO_4 %
3	Curaçao	0.00	0.26	0.00	23.2	0.01	0.03
146	Bone	0.03	0.45	0.12	20.4	0.32	0.78
147	Morocco	0.01	0.26	0.36	21.5	0.36	0.74
10	Florida pebble	0.10	0.64	0.64	20.4	0.96	1.10
16	Tennessee	0.16	1.70	1.76	19.8	2.44	2.80

The phosphates of iron and aluminum form a series of compounds of which some are acidic and may be crystalline (*9*), while others are basic and are noncrystalline. The former undergo decomposition in contact with hot water to form the amorphous basic compounds. Superphosphate is an acid material and the iron and aluminum phosphates which it contains must therefore be present in acidic combination. When a mixture of superphosphate and a potash salt is washed with hot water, iron and aluminum phosphates present will therefore decompose and be precipitated in an amorphous state in contact with the potash in the mixture. In this way the conditions are duplicated which were found to be effective in bringing about a retention of potash.

Iron and aluminum may occur in superphosphate in various combinations, some of which undergo no change on treatment with hot water, but the greater portion of each element is ordinarily present as the phosphate (*15*, *17*). If the loss of potash in superphosphate mixtures is due to the iron and aluminum phosphates in the superphosphate, a greater loss would be expected with superphosphates high in iron and aluminum than with those that are low in these constituents. In making tests to determine this relationship, the required quantities of potassium chloride and potassium sulfate were mixed with separate samples of cured superphosphates from different sources to give mixtures containing one part of K_2O to two parts of P_2O_5. The mixtures were adjusted to a moisture content of 7 to 8 per cent and stored in closed containers to prevent loss of moisture. After standing for one month the mixtures were washed with hot water (*1*) and the washed residues were analyzed for total potash by the J. Lawrence Smith method. The increase in the potash found in each residue over that in the washed residue of the corresponding superphosphate before treatment gives the portion of the potash that has been retained by the superphosphate. The results obtained, as given in Table III, show that the loss of potash varies greatly with superphosphates made from different types of rock; that the loss is greater when the mixture contains potassium sulfate than when it contains potassium chloride; and that there is a close correlation between the potash retained by a superphosphate and its total iron and aluminum content.

Table IV shows the potash that is rendered insoluble when potassium chloride is mixed with a cured superphosphate in different proportions. The results indicate that the loss of potash when expressed in per cent of the P_2O_5 in the superphosphate undergoes little change with change in the proportion of potash in the mixture. It follows, therefore, that the loss of potash, expressed in percentage of the total potash in the mixture, will increase as the proportion of K_2O to P_2O_5 in the mixture decreases.

The results given in Table V show that the loss of potash in mixtures that have been allowed to stand for a month before washing is greater than in day-old mixtures and that a loss of potash occurs in mixtures with old superphosphate as well as in those that contain fresh superphosphate. The values in the last three columns of the table represent the means of closely agreeing results obtained with several samples of superphosphate.

TABLE IV. LOSS OF WATER-SOLUBLE POTASH IN SUPERPHOSPHATE–POTASSIUM CHLORIDE MIXTURES

(Expressed in per cent of P_2O_5 in superphosphate)

K_2O/P_2O_5 in Mixture	Potash in Superphosphate Residue: Before treatment	After treatment[a]	Potash Rendered Water-Insoluble
Florida pebble superphosphate No. 54			
1:0.5	0.41	0.75	0.34
1:1	0.41	0.78	0.37
1:2	0.41	0.87	0.46
1:3	0.41	0.75	0.34
1:10	0.41	0.75	0.34
Tennessee superphosphate No. 56			
1:0.5	0.31	0.81	0.50
1:1	0.31	0.94	0.63
1:2	0.31	0.98	0.67
1:3	0.31	0.96	0.65
1:10	0.31	1.21	0.90

[a] Superphosphate mixed with potassium chloride and leached after 30 days.

TABLE V. VARIATION IN LOSS OF WATER-SOLUBLE POTASH IN SUPERPHOSPHATE–POTASSIUM CHLORIDE MIXTURES WITH AGE OF SUPERPHOSPHATE

(K_2O/P_2O_5 in mixture = 1 to 2)

Age of Superphosphate Used *Days*	Age of Mixture when Leached *Days*	Potash in Washed Residue[a]: Before treatment %	After treatment[b] %	Potash Rendered Insoluble[c] %
Florida pebble superphosphate				
30	1	0.36	0.50	0.28
600	1	0.50	0.65	0.30
4	30	0.09	1.27	2.36
30	30	0.36	1.02	1.32
600	30	0.50	0.75	0.50
Tennessee superphosphate				
30	1	0.57	0.80	0.46
600	1	0.84	1.28	0.88
4	30	0.17	0.85	1.36
30	30	0.57	1.35	1.56
600	30	0.84	2.06	2.44

[a] Expressed in per cent of P_2O_5 in superphosphates.
[b] Superphosphate mixed with potassium chloride and washed after 30 days.
[c] Per cent of total in mixture.

Table VI gives some results obtained when superphosphates were treated with a potash salt in various ways. The maximum loss of potash in these tests, amounting to 3.54 per cent of the total potash present, occurred when a mixture of a superphosphate with a saturated solution of potasssium sulfate was allowed to stand for 30 days, and then evaporated to dryness before leaching with water.

A superphosphate is allowed to cure for about a month on

TABLE VI. LOSS OF WATER-SOLUBLE POTASH IN DIFFERENT TREATMENTS OF A CURED SUPERPHOSPHATE WITH A POTASH SALT

(K_2O/P_2O_5 in mixture = 1 to 2)

Phosphate Sample	Phosphate	Treatment	Potash in Washed Residue[a] Before treatment	After treatment with: KCl	After treatment with: K_2SO_4	Total Potash Rendered Water-Insoluble by Superphosphate in Mixture with: KCl	Total Potash Rendered Water-Insoluble by Superphosphate in Mixture with: K_2SO_4
			%	%	%	%	%
10	Florida pebble superphosphate	Mixed with solid salt, washed at once	0.50	0.90	0.95	0.80	0.90
16	Tennessee superphosphate	Mixed with solid salt, washed at once	0.80	1.25	1.45	0.90	1.30
10	Florida pebble superphosphate	Mixed with solid salt, washed after 30 days	0.50	0.72	0.95	0.44	0.90
16	Tennessee superphosphate	Mixed with solid salt, washed after 30 days	0.80	2.05	2.20	2.50	2.80
12	Florida pebble double superphosphate	Mixed with solid salt, washed at once	0.30	0.32	0.33	0.04	0.06
13	Tennessee double superphosphate	Mixed with solid salt, washed at once	0.46	0.79	1.02	0.66	1.12
56	Tennessee superphosphate	Soaked in 10 per cent salt solution for 1 day and washed	0.31	0.62	0.74	0.62	0.86
56	Tennessee superphosphate	Soaked in 10 per cent salt solution for 30 days and washed	0.31	1.68	2.08	2.74	3.54
15	Tennessee double superphosphate	Soaked in 10 per cent salt solution for 1 day and washed	0.33	0.69	0.87	0.72	1.08
16	Tennessee superphosphate	Mixed with concentrated salt solution, evaporated to dryness after 1 day and washed	0.84	1.73	2.65	0.89	1.81
16	Tennessee superphosphate	Mixed with syngenite, evaporated to dryness after 1 day and washed	0.80	....	3.05	....	2.25

[a] Expressed in per cent of P_2O_5 in superphosphate.

an average before being used in fertilizer mixtures, and it is probable that fertilizer mixtures as a rule are a month old before being analyzed by the state control chemist. The average fertilizer mixture for the past 10 years contained a ratio of K_2O to P_2O_5 of 1 to 2. It may be concluded, therefore, from this investigation that the potash retained in the extraction of mixed fertilizers by the official procedure amounts on an average to about 1.5 per cent of the total potash present. The results further indicate that the loss of potash occurs for the most part as a result of the reactions taking place during the extraction of the sample for analysis and that there is no actual loss in the fertilizer value of the potash. The failure to recover all the available potash in fertilizer mixtures has meant a loss to the fertilizer industry of about 3200 tons of potash (K_2O) per annum, valued at $220,000.

Summary

The extraction of mixed fertilizers containing superphosphate as directed in the official procedure for determining available potash fails to recover all the water-soluble potash incorporated in the mixture as a result of occlusion or adsorption of a small portion of the potash in the basic iron and aluminum phosphates formed during the extraction.

The loss of potash varies with the iron and aluminum content of the superphosphate in the mixture and is greater when the mixture contains potassium sulfate than when it contains potassium chloride.

A loss of potash occurs in mixtures that contain an old superphosphate as well as in those that contain a freshly prepared superphosphate and the loss of potash in mixtures that have been allowed to stand for a month is greater than in day-old mixtures. For mixtures that are a month or more old the loss of potash amounts to about 1.5 per cent of the total potash present.

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Chemical Microscopy

IN THE Symposium on Recent Advances in Microanalysis at the New York Meeting of the AMERICAN CHEMICAL SOCIETY, C. W. Mason, of Cornell University, speaking on "Chemical Microscopy," limited his paper to the microscopical study of crystals and related physico-chemical phenomena, emphasizing that this field is of the greatest potential value to chemists who deal with solids in any way, since the microscope can be used as an instrument for determining numerous optical constants and also for the direct observation of "phase-rule" phenomena in one- or multi-component systems.

The optical tests used by microscopists in crystal identifications were demonstrated by microprojection with polarized light, and it was pointed out that the growing amount of available data on optical characteristics makes possible highly positive identifications or differentiations by using properties that are obtainable in addition to any chemical information that is at hand The application of such phenomena in the study of micellar aggregates was also illustrated; materials of this character often show marked variations in microscopical features with chemical or physical treatment, and excellent control tests are possible for studying chemical derivatives, swelling, stretching, or permeation of fibers or other substances of high molecular weight.

The physical chemistry of processes involving crystals was stressed as an important field for microscopical study, not only for the identification of the actual solid phases present in the system at any time, but also because the type of equilibrium diagram is often predictable or confirmable by a simple examination. Examples of solid solution, adsorption phenomena, freezing, allotropy, salt systems, and eutectics were shown, indicating how the microscope is an essential tool of the physical chemist.

Determination of Stibnite Sulfur in Ores and Minerals

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THE selective determination of sulfur present as antimony trisulfide in stibnite is impossible by drastic oxidation methods—e. g., Cushman's bromine and acetic acid method (*3*), or sodium peroxide or carbonate-nitrate fusion (*1*)—which yield results for total sulfur. Interference by free sulfur, sulfate sulfur, and acid-insoluble sulfides is avoided in the evolution procedure of McNabb and Wagner (*5*). This method is satisfactory for pure natural stibnite or for antimony sulfide obtained by liquation of ores, but when applied to low-grade ores which contain considerable amounts of other metallic sulfides partly or wholly decomposed by hydrochloric acid (galena, cinnabar, copper glance) it yields results which include sulfur from these impurities. McNabb and Wagner (*6*) suggested the separate determination of alkali-insoluble sulfide impurities in the residue from extraction of stibnite with hot aqueous sodium hydroxide, but if applied to low-grade ores this method would be unduly laborious and would not exclude interference by sulfide impurities soluble in alkali. The authors attempted the determination of sulfur present as antimony sulfide (and as other sulfides soluble in alkali and decomposable by hydrochloric acid) by extraction with hot aqueous alkali, acidification of the filtered extract, and application of the evolution procedure to the reprecipitated sulfides. Results were irregular and as much as 10 per cent low, no doubt because of air oxidation of the dissolved sulfo salts.

The method described below permits the direct determination of sulfur present as alkali-soluble sulfide. The sample is extracted with hot sodium hydroxide solution, and the resulting solution of antimonite and thioantimonite reduced by aluminum powder. This precipitates metallic antimony and leaves sulfur in solution as sulfide ion, the hydrogen incidentally liberated preventing air-oxidation. The sulfide sulfur is determined iodometrically by pouring the solution into a measured excess of standard iodine solution suitably acidified and titration of excess iodine with standard thiosulfate. The reactions involved are:

$$Sb_2S_3 + 6OH^- = {}^{\equiv}SbS_3 + {}^{\equiv}SbO_3 + 3H_2O$$
$${}^{\equiv}SbS_3 + {}^{\equiv}SbO_3 + 2Al^\circ + 6OH^- = 2\,{}^{\equiv}AlO_3 + 2Sb^\circ + 3H_2O + 3S^{=}$$
$$3S^{=} + 3I_2 = 3S^\circ + 6I^-$$

Procedure

Weigh out sufficient sample (200-mesh) to yield not over 0.03 to 0.04 gram of sulfide sulfur (about 0.2 gram of pure stibnite to 2 grams of low-grade ores). Transfer to a porcelain or alkali-resistant beaker, add 20 cc. of 2 *N* sodium hydroxide, and boil for 20 to 25 minutes. Record the quantities of alkali used here and in subsequent operations, so that the quantity of acid required for final acidification may be estimated. Decant the alkaline extract into a small suction filter, and wash the residue by decantation with hot 0.5 *N* sodium hydroxide, passing this also through the filter. Discard the insoluble residue.

To the alkaline filtrate add aluminum powder or foil and heat until reduction is complete; usually 0.3 to 0.6 gram of aluminum will suffice. Allow the precipitate of antimony to settle, and decant the liquid through the filter. Wash the residue by decantation with several portions of hot 0.5 *N* sodium hydroxide, passing each washing through the filter. The extraction is complete when a drop of the wash-liquid gives a negative test with a drop of lead acetate solution on a spot-plate.

Cool the combined alkaline extracts, and pour into a measured excess (20 to 40 cc.) of 0.1 *N* iodine previously diluted to 200 cc. and mixed with enough concentrated hydrochloric acid to yield a solution finally distinctly acid (1 to 2 per cent of free concentrated acid by volume). Titrate excess iodine with 0.1 *N* sodium thiosulfate, using starch indicator.

With rich ores a too prolonged grinding should be avoided, or air oxidation of some sulfide sulfur may occur. This precaution was not observed to be necessary with lean ores.

The quantity of aluminum required varies, much of the metal being dissolved with evolution of hydrogen. The reaction is less vigorous and is more readily controlled if aluminum foil is used. Aluminum powder acts more rapidly, producing considerable effervescence, which may become excessive if the powder is too fine.

If the sodium hydroxide contains traces of oxidized chlorine compounds the solutions should be treated with aluminum powder before use.

A blank test of the excess titration (last paragraph of procedure) showed no consumption of iodine when a sodium hydroxide solution reduced with aluminum was added to the acidified iodine solution and the iodine titrated with thiosulfate. The procedure described requires about 2.5 hours.

Tests of the Method

APPLICATION TO PURE STIBNITE. The accuracy of the method was tested by trials with a specimen of pure stibnite containing not more than traces of foreign sulfides, and analyzed also by the evolution method. The latter was used in a modified form, the hydrogen sulfide being absorbed in cadmium acetate solution, and sulfide sulfur determined by addition of potassium iodide and titration with 0.1 *N* permanganate; this avoided filtration of cadmium sulfide and the subsequent shaking with acidified iodine solution (*5*). Results by both methods appear in Table I.

TABLE I. DETERMINATION OF SULFIDE SULFUR IN PURE STIBNITE

	Modified Evolution Method %	Proposed Method %
1	28.05	28.00
2	28.09	27.98
3	28.17	28.20
4	27.99	27.95
5	27.95	28.10
	Av. 28.05	28.05

EFFECTIVENESS OF ALKALI EXTRACTION FOR SEPARATION OF ANTIMONY SULFIDE FROM FOREIGN SULFIDES. The specificity of the new method with respect to antimony sulfide in low-grade ores was tested (1) by examination of the behavior of various foreign sulfides in the alkali-extraction procedure, (2) by qualitative study of the effects of alkali extraction applied to artificial mixtures of stibnite and other sulfides, and (3) by actual determination of stibnite sulfur in such mixtures by the proposed method.

1. Solubility of Some Mineral Sulfides in Hot Aqueous Alkali. Cinnabar, copper glance, galena, molybdenite, zinc blende, and pyrite were found to be unattacked by hot aqueous alkali. By combined action of alkali and aluminum powder or foil the first three sulfides were completely decomposed, sodium sulfide being formed and the metal precipitated. The same treatment decomposed pyrite with difficulty and incompletely, with removal of only one atom of sulfur. Molybdenite and zinc blende were unattacked.

TABLE II. DETERMINATION OF STIBNITE SULFUR IN MIXTURES OF STIBNITE AND OTHER SULFIDES

Total Weight of Sample	Sb_2S_3	Foreign Sulfides PbS	Cu_2S	HgS	FeS_2	0.1 *N* Iodine	0.1 *N* $Na_2S_2O_3$	Sulfur Found	Stibnite Sulfur Present[c]
Grams[a]	*Gram*[b]	*Gram*	*Gram*	*Gram*	*Gram*	*Cc.*	*Cc.*	%	%
1.0000	0.1986	0.1013	0.1000	0.1004	0.1007	40.00	7.31	5.23	5.24
1.0000	0.2009	0.1008	0.1000	0.1002	0.0998	40.00	6.32	5.39	5.30
1.0000	0.1994	0.1002	0.0994	0.0996	0.1000	40.00	7.31	5.23	5.26
1.0000	0.2012	0.0998	0.1000	0.0981	0.1005	40.00	7.21	5.25	5.31
1.0000	0.0975	0.0972	0.0963	0.0968	0.1976	25.00	7.66	2.77	2.72
1.0000	0.1000	0.1000	0.0995	0.1004	0.1010	25.00	7.85	2.74	2.72
2.0000	0.0585	0.1003	0.0992	0.0983	1.0000	20.00	6.60	1.07	1.09
2.0000	0.0600	0.1018	0.1027	0.1006	0.9996	20.00	6.10	1.11	1.11
2.0000	0.0595	0.1020	0.1038	0.1000	1.0000	20.00	6.00	1.12	1.10
2.0000	0.0567	0.1015	0.1000	0.1001	1.0000	20.00	6.50	1.08	1.07

[a] Combined sulfides made up to weight indicated by addition of quartz sand.
[b] Specimen contained 25.60 per cent of stibnite sulfur.
[c] Includes previously determined traces of sulfur present as arsenic and antimony sulfides in the pyrite and cinnabar added to the samples.

2. Qualitative Tests of Hot Alkali Extraction of Artificial Mixtures of Stibnite and Some Other Mineral Sulfides. A mixture of 0.2 gram each of stibnite and the selected foreign sulfide was extracted first with 20 cc. and then again with 10 cc. of boiling 2 *N* sodium hydroxide, the residues being washed each time with hot 0.5 *N* sodium hydroxide and tested for antimony. The first extract was tested for presence of the foreign metal, and the second extract was tested also for antimony.

To test for mercury there was used the Feigl spot-test (*4*) with aniline and stannous chloride. Lead, copper, and iron were sought by addition of sodium tartrate and sodium sulfide. To examine for antimony in the second extract there was employed the Clarke and Evans color test (*2*) with potassium iodide, pyridine, and gum arabic.

These tests showed that antimony sulfide was completely dissolved by the first extraction, the second extract being free from antimony as were also the undissolved residues. Sulfides of mercury, copper, lead, and iron were unattacked in the first extraction, tests for these metals in the filtrates being negative. Only traces of lead, copper, and iron were detected in the second extract from mixtures of stibnite with galena, copper glance, or pyrite, respectively, and cinnabar was wholly undissolved.

3. Determination of Stibnite Sulfur in Artificial Mixtures of Stibnite with Various Proportions of Foreign Sulfides. Mixtures of weighed amounts of stibnite, galena, copper glance, pyrite, and cinnabar were diluted with quartz sand to simulate low-grade ores, and analyzed by the new method as described. Results are presented in Table II.

The results in Table II indicate that the proposed method permits accurate determination of the sulfur of stibnite in presence of sulfides of lead, copper, iron, and mercury. Free sulfur and arsenic sulfide interfere to whatever extent they are present, and will ordinarily introduce an inconsiderable error.

The new method is recommended for the rapid and accurate determination of stibnite sulfur in stibnite and in low-grade ores containing as impurities other sulfides such as galena, copper glance, cinnabar, and pyrite. It will probably yield the sulfur combined with antimony in certain mineral double-sulfides such as livingstonite, boulangerite, and zinkenite.

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Zinc Cobaltinitrite for the Detection of Potassium

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THE reagents commonly used for the qualitative detection of sodium and potassium are not completely satisfactory. Probably the most sensitive are sodium cobaltinitrite for potassium and zinc uranyl acetate for sodium as recommended by Kolthoff (*1*). If these are used, however, a separate portion must be used for sodium; and if a large amount of potassium is present it must be at least partially removed before use of the sodium reagent. For this purpose, the zinc perchlorate procedure of Reedy (*2*) is very satisfactory.

The purpose of this investigation was to develop a reagent which would retain the sensitivity of the sodium cobaltinitrite reagent without introducing sodium ion and at the same time leave the filtrate in a state best suited for the use of zinc uranyl acetate for the detection of sodium. Zinc cobaltinitrite should answer the purpose, since the added zinc ion should decrease the solubility of the sodium precipitate by common ion effect.

Experimental

Throughout the course of the investigation the chemicals used were Baker's C. P. analyzed. Attempts to prepare zinc nitrite were almost entirely without avail. Barium nitrite was made by metathesis of sodium nitrite and barium chloride. On dissolving this in a solution of cobalt nitrate and acidifying with acetic acid, a yellow precipitate of barium cobaltinitrite separated, and was converted to zinc cobaltinitrite by shaking with a solution of zinc sulfate. The resulting solution, however, was too unstable to be practical.

Direct preparation of a cobaltinitrite solution was then tried by passing oxides of nitrogen through (1) a solution of cobalt nitrate containing suspended zinc hydroxide, (2) a suspension of zinc and cobalt hydroxides, and (3) a solution of zinc acetate and cobalt acetate. In all cases a darkening resulted and the solution gave a yellow precipitate with potassium nitrate. The third method gave by far the most consistent results. The oxides of nitrogen were made by the action of either dilute sulfuric acid on a solution of potassium nitrite or concentrated nitric acid on copper, the latter being most convenient.

The final method of preparation adopted was to pass a rapid stream of oxides of nitrogen, made by the action of concentrated nitric acid on copper foil, through a solution saturated with both cobalt acetate and zinc acetate for from 45 to 60 minutes. The resulting dark brown solution was tightly stoppered, allowed to stand overnight, and then decanted from any precipitate. If kept tightly stoppered to prevent loss of oxides of nitrogen, the solution was as sensitive as ever after 6 weeks; left open to the air, all cobaltinitrite disappeared within a week.

To test the sensitivity of the reagent, solutions containing varying amounts of potassium nitrate were mixed with an equal volume of the reagent. The sensitivity is given in milligrams of cation per milliliter of the resulting solution. Repeated tests showed that 1 mg. of potassium per milliliter gave an immediate yellow precipitate. After standing for 15

minutes, from 0.4 to 0.6 mg. per ml. was the smallest amount detectable. Sodium in amounts up to 50 mg. per ml. seemed without effect on the sensitivity.

Solutions containing both sodium and potassium nitrates were treated with zinc cobaltinitrite until all the potassium was removed and then tested for sodium by zinc uranyl acetate reagent prepared according to Reedy (*2*). After removal of 50 mg. of potassium per milliliter 3 mg. of sodium per milliliter were detectable by the formation of a distinct yellow-green precipitate. When the amount of potasium was 10 mg. per milliliter, 1 mg. of sodium could be detected in the filtrate.

Procedure

To the solution from the alkaline earth group, which contains no barium, arsenate, phosphate, or ammonium, add an equal volume of zinc cobaltinitrite solution and let stand for 15 minutes. A yellow precipitate of potassium cobaltinitrite indicates potassium. Filter and to the filtrate add zinc uranyl acetate solution. Sodium is indicated by the formation of a crystalline greenish yellow precipitate.

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The Estimation of Starch

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THE estimation of starch is of interest to those engaged in many industries, to those concerned with the enforcement of food laws, and to plant chemists and physiologists in the investigation of botanical, horticultural, and agronomic problems. The objects to be attained by the various analysts, the degree of accuracy required, the methods which are most suitable, and the particular technical difficulties involved, vary. In the analysis of plant products for any constituent, a separate problem may arise for each type of material. This is true of starch analysis and each field of activity has its favored methods which are believed to be more suitable in their particular circumstances.

Starch is usually accompanied by other carbohydrate substances, such as cellulose, hemiculluloses, pentosans, gums, mucilages, glucosides, pectins, and tannins, and its own hydrolytic products, sugars and dextrins. It is the problem, of course, to separate starch from these substances, if possible, and, if not, to hydrolyze it to sugars in their presence under such conditions as will cause the least interference by these other materials.

Acid Hydrolysis

The simplest method of converting starch to sugar is the acid hydrolysis method. Approximately 90 parts of starch yield 100 parts of glucose. In practice, this yield, popularly considered theoretical, has not been obtained. What is the theoretical yield?

To the starch manufacturer, "starch" is everything in the granule (*17*). It has been customary, however, with those in other fields to consider starch as only that which on hydrolysis yields simpler carbohydrates. With the latter viewpoint the theoretical yield may be calculated from the organic structure of starch. If starch consists of a chain of glucose units linked together with the loss of water at each linkage, on hydrolysis there will be added to its weight one molecule of water for each glucose unit, less one. If the chain contains six, twelve, or twenty-four glucose units, the glucose starch conversion factors are, respectively, 0.917, 0.907, and 0.904. If the chain is longer, the conversion factor approaches more closely 0.9. If the chain is closed to form a loop, the factor is exactly 0.9, regardless of the size of the molecule. Recent contributions of organic chemists (*16*, *18*, *22*, and others) indicate that the chain is very long and the correct factor is therefore very nearly 0.9. However, the work of Noyes (*36*) indicates that 100 per cent recovery cannot be obtained by acid hydrolysis, and he accordingly suggests the factor 0.93. Others have adopted this and other factors. Noncarbohydrate constituents, moisture excepted, such as ash, protein, fat, and fiber, are rarely present in excess of 1 per cent in a good grade of starch, although these constituents and also moisture are not easily and accurately determined. It has been demonstrated that glucose is not injured by heating with acid unless excessive concentrations of acid or duration of heating are used (*5*, *8*). Nevertheless there have been formed from glucose by the action of acid and there also occur in the mother liquor of starch hydrolyzates in some industrial processes, disaccharides which are probably derived from glucose and have less reducing power than glucose. These factors probably account for the failure to obtain complete recovery of starch unless the larger factor, for which there is no theoretical basis, is used. Using the factor 0.9, the author has recovered, as measured by the reducing power of the glucose, 97 per cent of the starch.

Because of the susceptibility of other carbohydrates to attack by boiling acids, the use of this method has limited application. It has been discontinued by workers in most plant fields. The only recent attempt to utilize this method is that of Fraps (*15*) who used a very dilute acid (0.02 *N*) and completed the hydrolysis with stronger acid after the insoluble matter had been removed and corrected for pentosan dissolved.

Enzymatic Hydrolysis

When carbohydrate substances other than starch are present, it has been customary to resort to enzymatic hydrolysis. Diastatic, as well as other enzymic preparations, are notoriously impure and contain other enzymes which attack many other substances. Moreover these preparations do not hydrolyze starch into a single product, but rather into mixtures of sugars, or of sugars and dextrins. The relative proportions of these products are not constant but depend upon every possible variation in the conditions of hydrolysis. As a result of this situation, the estimation of starch by diastatic means has been resolved into three types of methods: (1) the mixed products obtained are estimated by two different methods, and each product may be calculated by the use of simultaneous equations; (2) empirical methods, by which the products are obtained under rigid conditions of hydrolysis and are found to have certain definite reducing or rotational values; and (3) methods in which the diastatic action is supplemented by a subsequent hydrolysis with mineral acids to yield a single product, glucose.

Barley and Malt Diastases

It is not possible here to consider all the diastatic methods. Granular starch consists mainly of two substances, α-amylose or amylopectin and β-amylose, or "amylose." Diastatic enzymes have been differentiated into two amylases, called α- and β-, according to the stereochemical form of the maltose produced (*27*).

The α-amylase presumably converts the amylopectin into dextrins and is referred to as the liquefying or dextrinogenic amylase. β-Amylase converts the amylose into maltose and is known as the saccharogenic amylase (*37*). Both enzymes are present in malt but only the β- in the ungerminated grain. Later work, however, indicates that both enzymes will produce both dextrin and maltose but at different rates (*35*), and that both enzymes are present in ungerminated grains, but in different amounts (*44*).

Ling, Nanji, and Harper (*30*) have suggested the use of the diastase of ungerminated barley. When this acts on the cereal starches the maltose formed is derived wholly from the β-amylose. Amylopectin yields a hexa-amylose (*31*) and a third constituent present in some starches, amylo-hemicellulose, is unattacked. The relative amount of maltose produced from the β-amylose is determined by a control experiment, using potato starch. Assuming that the ratio of amylose to amylopectin in cereal starches is fixed—namely, 2 to 1—the starch content may be calculated from the reducing power. However, other ratios of amylose to amylopectin have been reported (*26*, *41*, *42*).

The use of germinated barley is more common. Containing both types of amylases, it has both dextrin-forming and sugar-forming activity. Both amylose and amylopectin are attacked. The fate of amylo-hemicellulose is unknown. The products of this action are mainly maltose and in lesser degree dextrin, of varying composition. Under standard conditions the amount of maltose formed depends upon a group of factors referred to as the diastatic power of the malt. According to Ling (*29*), if a series of malt preparations which vary from 20 to 100 on his scale of diastatic power act upon barley and wheat starches, the amount of maltose which they will produce under identical conditions varies from 80 to 87.5 per cent of the weight of the starch. Therefore in making a determination on cereal products the yield of maltose obtained is compared with that theoretically produced by the same malt. Ling and others have contributed to quantitative methods based on this principle.

Another procedure involving the use of malt diastase and one apparently more in use in this country is that of heating the products of enzymatic hydrolysis with acids. By this means the maltose and dextrins are converted into glucose. The advantage of this procedure is that since glucose is the only final product arising from starch, it may be easily estimated. Also the extremely uniform conditions of hydrolysis required when a mixed product is produced are rendered less necessary. The chief disadvantage, as pointed out before, is that acid hydrolysis is not specific for starch or its hydrolytic products, maltose and dextrin. Other substances present may also be hydrolyzed, although the conditions of hydrolysis in this case are not as severe as those in the direct acid hydrolysis method. To avoid in part this disadvantage, various means have been employed to remove some of these contaminating substances. Simple filtration removes insoluble matter. Pectin material, but not dextrins, are precipitated by alcohol of a 60 per cent concentration. The Walton and Coe method (*45*), using this step, has been adopted as official by the Association of Official Agricultural Chemists (*3*). Herd and Kent-Jones (*19*) have recently published a criticism and comparative study of some of these methods.

Takadiastase

Takadiastase, the enzyme of the fungus *Aspergillus oryzae*, is widely used among workers in the field of plant physiology. Commercial preparations of this enzyme are mixtures of many enzymes (*34*), the pertinent ones being α-amylase and maltase. Davis and Daish (*6*) introduced it as a quantitative reagent and referred to Hill (*21*) as the authority that its products are maltose and glucose and that it does not give rise to resistant dextrins. Though the publications of Hill do not furnish any definite proof of such products, the statement has been repeated in many publications. Davis and Daish followed the course of the hydrolysis of starch and made periodical determinations of the optical rotation and the copper reducing power. Six hours from the start no dextrins were present. Assuming that the products were glucose and maltose only, they calculated that at 6 hours the ratio between the two was 0.1, and this ratio gradually increased to 6.0 at 72 hours. After 72 hours no further hydrolysis of maltose to glucose took place. The sum of the two constituents at any time was practically equivalent to the amount of starch originally present. Horton (*23*) was unable to duplicate these results and believed dextrins were present. However, the use of takadiastase has persisted and many methods have been proposed to determine the amounts of each of the sugars present. Thomas (*43*) found that at 24 hours the ratio between glucose and maltose was 2 to 1, but Widdowson (*47*) found higher proportions of glucose. Horton's data had previously shown that an increased concentration of enzyme gave a higher proportion of glucose, but Collins (*4*) pointed out the necessity of a high concentration of enzyme which, together with a sufficient length of time and the proper hydrogen-ion concentration, gave complete hydrolysis to glucose. Collins bases her conclusions on the fact that both takadiastase and acid gave a recovery of 93 per cent of the dry weight of the starch. Acid hydrolysis will give, however, a higher yield than 93 per cent, if the factor 0.9 is used to convert glucose to starch. If the factor 0.93 is used as she suggests, a recovery of nearly 100 per cent should be obtained.

Denny (*7*) and Lehmann (*28*) report complete recovery of starch by this method.

If both maltose and glucose are present during the hydrolysis, and if present in the proportions that have been reported, it should be possible to detect the maltose. According to Davis and Daish, there were ten times as much maltose as glucose present at 6 hours, three times as much at 12 hours, and one-fourth as much at 48 hours. According to Thomas, at 24 hours, there was one-half as much maltose as glucose. Working with mixtures of pure glucose and maltose, the author has been able to identify the osazones of maltose when it was mixed with three parts of glucose. The total sugar concentration of the solution was 10 per cent. With lower concentrations or with higher proportions of glucose, the osazones of maltose could not be detected in the presence of those of glucose. When these tests were made upon the hydrolyzate from starch, no maltose was detected at any time, even at the early stages of hydrolysis when the proportion of it should be high. The enzyme was killed and the solution concentrated before making the test so that the conditions were comparable to those with pure sugars. Precipitation of the enzyme material with alcohol did not alter the results.

Hill (*20*) described a method for the isolation of maltose when mixed with glucose by the use of maltase-free yeast, but he did not report having used it on the products of takadiastase action. Englis, Pfeifer, and Gabby (*11*) suspected that some other disaccharide than maltose was present in the hydrolytic products. The failure of the attempt to identify maltose does not prove its absence nor would the proof of its absence invalidate the use of takadiastase. If, however, the

intermediate product were some carbohydrate other than maltose and could be identified, means might be found to hasten its hydrolysis.

The use of takadiastase is widespread among plant workers and thus deserving of attention. The preparations, however, contain many enzymes which attack other insoluble carbohydrates than starch. Thus after enzymatic hydrolysis, in addition to maltose and glucose, there are many other substances in solution. Some of these are readily removed by clearing agents. The maltose may then be hydrolyzed by acid to glucose, the wisdom of which step was pointed out before, or each sugar may be determined separately by many combinations of methods which have been proposed.

Denny (*7*) has recently published detailed directions for converting starch to glucose quantitatively without the necessity of acid treatment. The author has used this method on a number of different types of plants and obtained lower results than when the takadiastase was supplemented with acid hydrolysis. This difference in results is probably not due to the incomplete hydrolysis of the starch by either of the methods. It is probably due to the high results obtained when acid hydrolysis takes place on substances not derived from starch. However, even the lower of these results is undoubtedly higher than the true starch content.

Chemical and Physical Methods

There are other types of methods which have appeared for many years in isolated cases but which only recently have obtained recognition. These methods involve the isolation of the hydrolyzed starch by making use of some of its chemical and physical properties. Starch is dissolved by many reagents with a greater or less alteration in its physical properties, but apparently with little hydrolysis. Reagents which have been used for this purpose are various organic and inorganic acids, alkalies, salts, and glycerol.

The solubility of starch in cold and relatively concentrated hydrochloric acid is the basis of a method by Rask (*38*). The starch is dispersed into a clear or slightly opalescent but filtrable solution, out of which it can be precipitated quantitatively by alcohol. According to Rask, "Starch seems to undergo no deep-seated changes in the process of acid dispersion, followed by alcoholic coagulation. It still gives the characteristic blue color with iodine and it has no reducing action on Fehling's solution. The only noticeable changes in the starch are that the original morphology or identity of the grains has been destroyed and that the starch itself has been rendered water-soluble." The starch which is precipitated by alcohol is collected on a filter and weighed. The method has received considerable attention in the analysis of whole wheat, flour, and bran, and has been adopted as a tentative method by the Association of Official Agricultural Chemists (*1*).

Collaborative work in this association indicates that this method needs considerable study and perhaps modification. Conflicting statements appear as to the relative yields obtained by this method in comparison with various diastatic methods (*19, 24, 39*). Ling and Salt (*32*) believe that hydrolysis of starch occurs. Denny (*8*) presents data which indicate that the method tends to give low results by incomplete extraction of the starch from flour and also high results by inclusion of nonstarch substances in the alcoholic precipitate. He proposes that, after gelatinization with water, four extractions be made with acid to dissolve the starch and that the precipitate obtained later by alcohol be hydrolyzed with takadiastase. He also applied the procedure to leaf material, using both hydrochloric and sulfuric acids as the starch solvents.

The author attempted to apply the Rask procedure to the analysis of starch in woody material containing large amounts of hemicelluloses, although Rask made no claims as to the adaptability of the method to such material. The acid caused the evolution of such a large number of gas bubbles, presumably of carbon dioxide from the decomposition of uronic acid groups, that the making of the solution to volume with any degree of accuracy was impossible.

Precipitation of Starch Iodide

The large number of methods which have appeared for starch analysis is alone evidence of the unsuitability of any one of them for more than limited use. The field of plant analysis probably presents the most difficult problems for in the leaves, stems, and seeds of plants occur a variety of forms of carbohydrates. Many plant workers customarily check their quantitative results for starch with the qualitative iodine test and hope for but do not always obtain some correlation. The iodine test is fairly specific for starch in that few other substances giving this test are present in plants. The complex formed by the absorption of iodine by dissolved starch may be salted out of solution. If this precipitate could be collected free from other carbohydrate material and estimated by some appropriate method, the results would of course be readily correlated with the iodine test.

This type of method, first proposed by Kaiser (*25*) received impetus from the work of von Fellenberg (*12, 13, 14*), who dissolved starch with hot calcium chloride solution and precipitated it from this solution with iodine. A number of similar methods applied to cereal products have since appeared (*2, 10, 33, 40, 46*, and others). Denny (*7, 9*) applied the method to plants and determined the amount of the starch precipitated first by titration of the iodine and later by hydrolyzing the starch to glucose with takadiastase.

The author has attempted to apply this method to the analysis of woody plants. There are two main steps in the isolation of the starch—namely, the extraction of the starch from the ground woody material and the precipitation of the starch from solution with iodine. There are two methods of obtaining a calcium chloride extract of the starch. One procedure is to extract the sample successively with small amounts of the salt solution until experience has shown that no more starch is removed. This probably ensures complete extraction but is tedious. Another procedure is to make one extraction with calcium chloride solution, to dilute the solution to a definite volume, and by removing the insoluble residue, obtain a clear extract. An aliquot of this can then be used for further work. It was found that this latter procedure would give results similar to the one of successive extractions only if the concentration of calcium chloride was sufficiently high. Long boiling was necessary in coarsely ground samples but not in those finely ground. The drastic conditions which are necessary to extract all the starch from woody plants may not be necessary in more succulent plants or in cereal products.

The second step in the method is the precipitation of the starch from the solution with iodine. This had been done directly in the calcium chloride extract, the calcium chloride acting as the salting agent. However, in using an extract of woody plants, this precipitation was found to be unreliable, and the precipitate, if obtained, had a tendency to run through the filter. If, however, the starch is precipitated from solution with alcohol, in which calcium chloride is soluble, it may be redissolved in water and again precipitated by iodine in the presence of some other salt. Ammonium sulfate was found to be very favorable for this precipitation, giving starch iodide particles which settle rapidly and may be easily retained on a filter. This precipitate may then be hydrolyzed by acid to glucose. The extra step involved in precipitating the starch twice does not lengthen the method, as

time is saved at other points. The double precipitation removes sufficient impurities from the starch so that the usual preliminary extraction of the plant to remove sugars and the usual final treatment with clearing agents are unnecessary. This method gives lower results in all types of plants than other starch methods and is believed to give a more accurate value for the true starch present.

Summary

The large variety of methods which exist for starch estimation bring out the fact that few of them are reliable even in limited cases. Neither acids nor diastatic enzymes are sufficiently specific for accurate results. The development of highly purified and specific enzymes may solve the problem. Methods based on other chemical and physical properties of starch, such as its solubility in salts and acids, and its insolubility in iodine and salt solutions, deserve closer study and no doubt many contributions will be made in the future along such lines.

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Determination of Alkalies in Feldspars

A Modified Hydrofluoric Acid Method

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MUCH time and effort have been expended upon investigations of the possibility of replacing the time-honored J. Lawrence Smith (*8*) method for the disintegration of silicates, preliminary to the determination of the alkali metals, sodium and potassium, by a more expeditious procedure.

Because of the ease of initial decomposition of the silicate sample by means of hydrofluoric acid, possible modifications of the original Berzelius (*1*) method—in the direction of the elimination of the undesirable conversion of sulfate to chloride by means of barium chloride—have long intrigued the analytical chemist. Low (*5*) and later Krishnayya (*4*) modified some portions of the method but did not successfully eliminate the particularly objectionable sulfate-chloride conversion. Scholes (*7*) described an excellent modification which eliminated most of the undesirable features of the original method and yet took full advantage of the hydrofluoric acid disintegration. The method gave results of good accuracy and precision with a considerable reduction in the amount of time necessary for analysis. Unfortunately, the procedure required a prohibitive amount of direct supervision and has therefore never become popular for routine determinations.

The method devised by Knowles and Redmond (*3*), wherein the alkali metals are isolated as mixed chlorides after removal of aluminum and calcium as quinolate and oxalate, respectively, is productive of excellent results. The only objectionable feature of the method is the fact that, in materials with as high a percentage of aluminum as feldspar, the removal of this component with 8-hydroxyquinoline is extremely burdensome unless a relatively small sample—0.1 to 0.2 gram—is used. The use of a small sample does not appreciably affect the accuracy of the total chloride determination, if reasonable attention is paid to the details of the method. However, the ultimate separation of the sodium and the potassium, when working with small samples, is uncertain by most of the gravimetric methods now available, unless an unreasonable amount of time is expended in their recovery. This is true regardless of the method of separation—perchlorate, chloroplatinate, or triple acetate—because of the solubility factors affecting one or the other of the alkali salts, depending on the method chosen for the separation.

After a thorough investigation of each of the foregoing methods, a further modification of the Berzelius method was evolved. Volatilization of silica as tetrafluoride is unnecessary if complete removal can be accomplished by other means. This eliminates the necessity for the introduction of sulfuric

acid and its subsequent questionable removal with barium chloride. Hostetter (*2*) has shown that aluminum, iron, and magnesium can be precipitated as hydroxides by the addition of calcium oxide, which will also precipitate the fluorine as calcium fluoride. The silica can also be quantitatively removed as silicofluoride. Removal of calcium is accomplished by means of ammonium carbonate and ammonium oxalate and the alkali carbonates are converted to chlorides with hydrochloric acid.

Table I indicates the accuracy of the method when compared with the J. Lawrence Smith procedure which was used as standard throughout this investigation.

Table I. Accuracy of Method

Sample	J. Lawrence Smith	Modified Procedure	Error
	Gram[a]	*Gram*	*Gram*
70	0.1220	0.1222	+0.0002
99	0.1042	0.1040	−0.0002
M4072	0.0825	0.0825	±0.0000
M4084	0.1087	0.1087	±0.0000
B749	0.1128	0.1125	−0.0003
B753	0.1077	0.1077	±0.0000

[a] National Bureau of Standards certificate value.

No unusual apparatus or reagents are required, though a good supply of platinum ware in the form of medium-capacity dishes is effective in reducing analytical time to a minimum when a large number of determinations are necessary.

Reagents

Hydrofluoric acid, 48 per cent. A commercial c. p. reagent was used.

Calcium oxide. The ignition product of a specially purified reagent calcium carbonate was used. (Early in the investigation, erratic results for total alkali chlorides were encountered. They were traced to the calcium carbonate used, which was found to contain a considerable amount of sodium.) The reagent is purified by the method suggested by Schaal (*6*): A quantity of the reagent is repeatedly digested with fresh quantities of distilled water, the salt being finally dried and ignited to the oxide. A small correction, the extent of which can be found through analysis and which should not exceed 0.5 mg. when working with 0.5-gram samples, is to be deducted from the value obtained for total chlorides. This represents the amount of sodium, as chloride, which has escaped extraction during the purification process.

Ammonium carbonate. One hundred grams of a c. p. reagent are dissolved in 80 ml. of ammonium hydroxide (sp. gr. 0.9) and diluted to 500 ml.

Ammonium oxalate. A saturated solution of a calcium-free reagent is used.

Procedure

Transfer 0.5 gram of the −150-mesh sample (previously dried at 110° C.) to a 75-ml. platinum dish (a dish of the Payne type is particularly suitable) and moisten with water. Add an excess (10 ml. is sufficient) of hydrofluoric acid and evaporate the solution to dryness on the water bath. Take up the residue with water (complete solution is unnecessary) and transfer to a 100-ml. beaker, to which approximately 2.5 grams of purified calcium oxide have been added. Police and rinse the dish, adding the washings to the beaker. Stir, and after boiling briskly for 5 minutes, filter through a retentive paper, catching the filtrate in a 300-ml. porcelain casserole or platinum dish. Police the beaker and add the rinsings to the filter. Wash the precipitated hydroxides and fluorides several times with boiling water and discard the residue.

Add 25 ml. of ammonium carbonate solution to the filtrate and evaporate to dryness. Take up in a minimum of water, add 15 ml. of the ammonium carbonate solution, and allow to digest for 15 minutes. Filter through a retentive paper, catching the filtrate in a 100-ml. beaker. Wash the residue sparingly with cold water and discard.

Treat the filtrate with 4 drops of ammonium oxalate and digest, while uncovered, at a temperature just below the boiling point for 1 hour. The solution is now reduced in volume to about 50 ml.

Filter through a tight paper, catching the filtrate in an untared platinum dish, and wash the residue well, but sparingly, with a 1 per cent solution of ammonium oxalate. Discard the residue and after treatment with an excess of hydrochloric acid (to convert carbonates to chlorides), evaporate the filtrate to dryness on the water bath.

The ammonium salts are completely volatilized at a low temperature (below dull redness) and the salts just melted. Dissolve the residue in a minimum of water and filter through a small paper, catching the filtrate in a tared platinum dish. Wash the residue sparingly with cold water and discard. Add a few drops of hydrochloric acid to the filtrate to convert any alkali carbonates to chlorides and repeat the evaporation. Just melt the salts over a very low flame and desiccate over an active desiccant. Weigh rapidly (alkali chlorides are relatively hygroscopic) and record as total alkali chlorides. Reserve the residue for the determination of sodium and potassium.

The nonvolatile matter removed by filtration after the first volatilization of the ammonium salts is of no great consequence, amounting to only 0.7 mg. (±0.4 mg.). In any but the most exacting analysis this step in the procedure can be eliminated entirely by weighing the total alkali chlorides plus nonvolatile matter and correcting for the latter.

Summary

A further modification of the Berzelius method for the disintegration of a silicate, preliminary to the isolation of the alkali metals as chlorides, has been successfully employed in the analysis of feldspar.

Replacement of the J. Lawrence Smith procedure by the modified method entails no sacrifice in analytical accuracy and reduces the time required for an analysis. Reagent costs have been reduced and a more economical use of equipment has been attained. Possibilities of the application of the method to the analysis of other ceramic materials and products are encouraging, though they have not been investigated.

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Microchemistry in Industry

At the Symposium on Recent Advances in Microanalysis, presented at the New York meeting of the American Chemical Society in April, 1935, under the chairmanship of Beverly L. Clarke, Frank Schneider, of Rutgers University, spoke briefly on "Microchemistry in Industry." He reported the results of a survey made to discover the extent to which micromethods were being used in industrial laboratories in this country. A surprising number of concerns were found to be making use of the principles of microchemistry to some extent. He pointed out that a closer coöperation between teachers of microchemistry and industrial laboratories would increase this number, and would reduce the number of cases where micromethods are tried and abandoned owing to faulty understanding of fundamental principles. He proposed the organization of a microchemical society.

Modified Methods of Analysis of Commercial Oil Emulsions and Suspensions

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Because of the complexity of types of commercial emulsions and suspensions, they are classified as (1) oil emulsions free from suspended solids, (2) oil emulsions containing suspended solids, (3) oil solutions and suspensions, and (4) water-base wax emulsions.

By far the majority of commercial insecticides, polishes, waxes, cosmetics, etc., can be analyzed in one of these four classes by the systematic procedures outlined. An important advantage is that in general preliminary drying to total solids is eliminated and therefore oxidative changes in properties are avoided.

EMULSIONS, good, bad, and mediocre, are to be found in increasing numbers as industrial products, and require methods of analysis which will be adequate to meet their growing complexity and at the same time satisfactory for reasonably general application to complex products. The methods herein outlined have been developed over a period of years in the authors' laboratory as a result of frequent use on complex industrial mixtures. There is no body of organized knowledge generally applicable in the literature; methods are known for such stable emulsions as milk, but do not provide for the complexity of introduction of other ingredients such as pigments, mineral oil, etc.

In the methods commonly employed for complex mixtures, the first step is usually to obtain the nonvolatile fraction and work on it. In practice this nonvolatile fraction is often far from solid and rarely attains constant weight. Some part of the oils present commonly evaporates more or less slowly, the emulsion often cracks during evaporation to give a layer of water under a layer of oil, and as a result the oil is apt to spatter during further evaporation. Any unsaturated oils present are partially oxidized and their constants altered so that identification is made uncertain.

The modified methods proposed obviate these defects and in the majority of cases permit a complete analysis on a relatively small sample. The methods have all been in use for an extended period, and are applicable to furniture and automobile polishes, cosmetic emulsions, water-base waxes, and petroleum emulsions used as insecticides, to mention only a few examples.

As is so often the case, the method of analysis to be applied depends to a large extent on some knowledge of the composition of the sample. The classification usually requires some preliminary qualitative work, unless the approximate composition is already known. In general, the products are first classified in one of four groups: oil emulsions free from suspended solids, oil emulsions containing suspended solids, oil solutions and suspensions, and water-base wax emulsions. Since many well-known methods are used and the procedures outlined are a combination of such known methods, many details have been omitted.

Oil Emulsions Free from Suspended Solids

These vary somewhat in composition, although they are mostly white emulsions, unless artificial color has been added. It is immaterial whether they are of the water-in-oil or of the oil-in-water type. Mineral oil is generally present, and may include volatile types such as turpentine substitutes. Sulfonated oil, in most cases sulfonated castor oil, may be used in greatly varying amounts. Saponifiable oil may be present. Frequently 1 to 2 per cent of soap is present. Ammonia soap is a favorite, though sodium, potassium, and triethanolamine soaps are also commonly used. Gums, in large and small quantities, often contribute to the stability of the emulsions. Wax may be present in very small amounts, in quantities not ordinarily identified. Larger amounts of wax in polishes are shown by experience to dull the luster of the surface. Wax is often present in relatively large quantities in cosmetic emulsions or in distinctly waxtype preparations, in which case a different method is used.

The presence or absence of sulfonated oil should first be definitely established. Mix 10 cc. of the original sample with about 1 cc. of concentrated hydrochloric acid. Filter half of this. Boil the balance of the acidified sample for a few minutes and filter, testing the two filtrates with barium chloride. The presence of a substantial amount more of sulfate from the boiled sample establishes the presence of sulfonated oil in the sample. The blank shows the possible presence of sulfate in the original sample, and may be omitted if sulfate is known to be absent. As a very small amount of sulfonated oil may give no noticeable amount of sulfate precipitate by this method, in special cases ash carefully with Eschka mixture, extract with water, and test the extract for sulfate.

METHOD. To 25 cc. of the sample in a narrow-necked graduated cylinder, add 0.5 cc. of concentrated hydrochloric acid. Shake thoroughly. Frequently the emulsion is broken and on standing will separate into two or more layers, the upper consisting of the mineral oil, the lower of the water and hydrochloric acid, and gums if present. It is usually more satisfactory to centrifuge the cylinder, when a clean-cut separation results. Any soap present is decomposed by the acid and the resulting fatty acid is in the oil layer.

If sulfonated oil or castor oil is present there may be three layers, the sulfonated and saponifiable oil often forming a layer between the other oil and the water. With chlorohydrocarbon present, the sulfonated or castor oil layer may be on the bottom, and in any event will be easily recognized by its different color and consistency.

Treatment in this way with hydrochloric acid does not split off any sulfate or sulfonate radical from the sulfonated oil, as would occur with a somewhat different procedure (*3*), commonly used for decomposition of sulfonated oils and requiring prolonged refluxing with acid.

The amounts of the separate layers are read directly, with an accuracy depending on the type of graduated equipment used. For rapid comparisons on products of known types, this is sufficient but normally more complete determinations are required.

Separate the layers in a separatory funnel as completely as possible, saving each layer. Frequently this is done on a larger sample to obtain more oil for identification, but it may be carried out on the same sample.

Wash the oils with water and add the washings to the aqueous portion. Separation in the separatory funnel can be greatly facilitated by immersing in a hot water bath. It is best to refrain from heating until most of the acid has been removed, thus

avoiding possible hydrolysis of any sulfonated oil present. After all the water is separated, the oil fraction must be cooled, as sulfonated oil is far more soluble in mineral oil in the hot than in the cold. Sufficient amounts of the mineral oils and sulfonated or castor oil are thus obtained for the determination of constants. If the castor oil has separated, data are obtained on the oil so separated. If the saponifiable oil present proves to be miscible with the mineral oil, the determinations are more involved and it is preferable to use a modified method, described below.

Obtain the saponification value of the supposed mineral oil. If it is substantially zero, get the specific gravity and viscosity as means of identification. The viscosity can be conveniently and rapidly obtained on the small amount of oil usually available by using an apparatus previously described (*1*).

If the supposed mineral oil contains saponifiable matter, obtain the acid value. A substantial acid value at this point indicates that soap was present in the original sample. Confirm this qualitatively by adding phenolphthalein to the diluted original sample. Soaps of alkalies and ammonia have an alkaline reaction, unlike soaps of triethanolamine. If soap is present, extract a saponified portion containing excess alkali with ether to obtain a purified mineral oil for viscosity and specific gravity determinations.

Saponification value, acid value, specific gravity, iodine value, refractive index, and solubility in alcohol will identify the separated saponifiable oil, which is normally castor oil, frequently of a blown grade. All these values may be obtained on 2 to 3 grams, or even less, of oil. The specific gravity is determined in a small pycnometer. Wash the oil out of the pycnometer with neutral alcohol and titrate it for acid value. After evaporating off most of the alcohol, add alcoholic potash and determine the saponification value in the usual way. The iodine value and refractive index may be obtained on less than 0.5 gram of the oil.

If sulfonated oil is present, in addition to saponification value, acid value, and specific gravity, also determine the organic sulfates by the Hart-Grimshaw method (*3*). When only a small amount of separated sulfonated oil is available, this can be done on a portion of the original sample after neutralizing the soap and any other alkalinity present. In this case the total organic and inorganic sulfates may be precipitated with barium chloride from the water solution after the determination, giving further information as to the type of sulfonated oil. This, together with estimation of solubility in alcohol and water, is usually sufficient to identify saponifiable and/or sulfonated oil. Sulfonated oils have no very definite limits of composition, though efforts at standardization are being made.

Evaporate to dryness an aliquot of the aqueous solution from the original separation. Ammonium chloride from ammonia soap will evaporate in the oven. Loss in weight on low-temperature ashing gives the weight of gums. Boil off the excess hydrochloric acid from another portion of the aqueous acid solution and precipitate the gums with alcohol. Identify the gums so precipitated by the usual tests (*4*).

Determine soap by direct titration of a portion of the original sample, correcting for any alkali or alkaline salts present. A good end point is nearly always obtained. Titration of the ash is misleading as, if sodium or potassium soaps are present with sulfonated oils, a considerable part of the ash is sodium or potassium sulfate. Determine ammonia by distillation with sodium hydroxide after adding calcium chloride, and triethanolamine by calculation from a Kjeldahl nitrogen determination on the original sample. The latter will occasionally require a correction because of a gumlike nitrogenous emulsifier.

The amount of fatty acids liberated from the soap by the hydrochloric acid is usually too small to affect the constants of the oils materially. Allowance can be made for them if necessary when interpreting the constants.

The foregoing method of separation is satisfactory in most cases. Very occasionally, however, the oils do not separate or the separation is not satisfactory. In that case an alternative method is applied.

Alternative Method. To 16 cc. of the sample in a 25-cc. narrow-necked graduated cylinder, add 8 cc. of 95 per cent alcohol. Make distinctly alkaline with sodium hydroxide solution, shake thoroughly, and centrifuge. The mineral oil separates on top and can be read by volume; sulfonated oil goes with the alkaline alcohol and water layer. Transfer to a separatory funnel and return the alcohol-water solution to the cylinder. Wash the mineral oil with 5 cc. of 50 per cent alcohol and add the washings to the cylinder. Render the alcohol-water solution just acid with hydrochloric acid. Sulfonated oil, if present, separates and its volume can be read. It is not usually necessary to centrifuge.

A determination of sulfates on the alcohol-water solution after liberation of the sulfonated oil and on the separated mineral oil shows practically no sulfate present in either case. This indicates that under these conditions, sulfonated oils can be treated with both sodium hydroxide and hydrochloric acid without splitting off the sulfate radical. Constants on the separated oils are determined as before.

Occasionally mineral oil is found emulsified in water by a large amount of gum; the oil may be extracted with ether from the original sample and determined by methods given above.

Oil Emulsions Containing Suspended Solids

Such emulsions in the main consist of a low-viscosity mineral oil, saponifiable oil, often a blown oil, and a suspended pigment or abrasive such as zinc or titanium oxide, diatomaceous earth, or a soft silica. They frequently contain more or less glycerol and usually an emulsifier. Gums of different types are nowadays being used more and more as emulsifiers for this type of emulsion. Small quantities of sulfonated oil and amyl acetate, oil of citronella, turpentine substitute, or other cover-odor complete the picture. Alcohol is occasionally added, together with any little pet ingredient that the manufacturer thinks makes his product superior to all others.

Method. Weigh a 50- to 100-gram sample into a centrifuge bottle. Add 50 cc. of ethyl ether and shake well, but not vigorously. Very stubborn ether-water emulsions, if formed, can generally be broken by directing a small stream of alcohol from a wash bottle around the outer surface of the emulsion (*2*). Separate with the centrifuge. Decant the ether and water layers into a separatory funnel, taking care that they do not become reëmulsified, and return the water layer to the centrifuge bottle. Alternatively, the ether may be siphoned from the centrifuge bottle, but this is difficult without also transferring some of the water layer. Repeat the ether extraction three more times using the same procedure. Wash the combined ether extracts twice with 20-cc. portions of water and add the washings to the water in the centrifuge bottle. Transfer the ether extract to a fat-extraction flask and distill off the ether, which is conveniently recovered in an empty Soxhlet extractor. Place the fat-extraction flask and contents in the oven for the minimum time necessary to drive off the residual ether. Filtration through a paper wet with ether, before evaporation, eliminates any water which could cause spattering in the oven.

The residue from the ether extract often consists of an upper layer of mineral oil and a lower layer of castor oil. To get a satisfactory separation for most practical purposes, cool the oils in ice water, adding cold ethyl ether and carefully but quickly decanting. Repeat this twice more. A little practice will enable one to make a good separation of the mineral oil from the castor oil, which if blown is very thick when cold. Should extreme accuracy be required, use the method of separation by means of caustic soda–alcohol–hydrochloric acid described above.

Identify the mineral oil and the saponifiable oil as in the previous method. If sulfonated oil is present only as a minor ingredient, as is commonly the case in this type of emulsion, it will not seriously affect the constants of the saponifiable oil.

The centrifuge bottle still contains the water solution and pigment or abrasive. Centrifuge and decant the water solution. Repeat this operation with hot water 3 to 4 times, shaking thoroughly each time. The number of times this need be repeated depends on the clarity of the last water extract. Some gums are only very slowly soluble. Combine the aqueous washings and evaporate to a small volume over a Bunsen burner. Finish on a water bath and finally in the oven until fuming just commences. Cool and weigh. This gives the combined weights of glycerol, gums, and any other water-soluble ingredients.

Add alcohol, stir well, and heat. Filter and wash the residue of gums and any other alcohol-insoluble materials with hot alcohol. Dry in the oven and weigh on a tared filter paper. The difference is glycerol, soap if present, and any other alcohol-soluble materials. The alcohol may be evaporated and glycerol determined in the residue. Soap may be titrated in diluted solution. Dissolve the gums in water and determine their identity (*4*). In examining the gums, starch should be considered as in the same group.

The gums and glycerol are separated individually by this method. Ether extraction of the total solids in the authors'

experience always carried over some of the glycerol, so that three layers were obtained from evaporation of the ether extract. There is then no simple means of knowing whether or not all of the glycerol had been carried over by the ether, in which the results indicate that it is slightly soluble. The gums remained with the pigment or abrasive and were usually determined by loss on ignition. This was not fully satisfactory, among other reasons because it did not allow of identification.

The moist pigment of abrasive remains in the centrifuge bottle, and may be dried *in situ* in the oven, brushed out, and weighed. The normal procedure is to make a mesh analysis, using 200- and 325-mesh sieves, and save the part meshing between these two for microscopical examination. This will at once determine whether the abrasive is a diatomaceous earth or a silica, and of what type. The pigment or abrasive may then be used for a mineral analysis if necessary.

This completes the analysis using a single sample. Each of the main ingredients has been individually separated unaltered in character. Alcohol or other water-soluble solvent, if present, may be determined by the usual distillation method on another original sample.

Oil Solutions and Suspensions

This type of product is not usually a true emulsion. The amount of water is very small, if present at all. If no water is present, the product in general has no dispersed liquid phase to fall in the emulsion class. Emulsions that have naphtha as an external phase but contain a substantial amount of water are not included in this class. That type, sometimes referred to as a reversed phase emulsion is classified like a similar emulsion with water as the external phase.

The term "oil" is used here as a designation for any distillable fraction from petroleum, such as naphtha, gasoline, kerosene, etc., or a corresponding coal-tar fraction, such as toluene, xylene, cumene, high-flash naphtha, etc. Ammonia soap is commonly present in this type of emulsion. Other soaps are rarely employed because of their adverse effect on the consistency of the final product. Analysis of this type of product is relatively simple because of the limitations on the materials apt to be present.

Method. Weigh a 100-gram sample into a distilling flask. Add solid calcium chloride in sufficient quantity to react with all the soap present. Without this addition to prevent foaming, distillation is often impossible. Determine the distillation range by the usual procedure. Care must be exercised to distill over all the oil without decomposing any compounds of fatty acids. Distillation from an oil-bath may help but usually is not necessary and it is easier, with proper manipulation, to distill the last fractions using a bare flame.

Any water present, such as from aqua ammonia used in making ammonia soap, distills over with, and separates from, the oil, and its amount can be read off as a check. Ammonia if present also distills over. The amount of oil is read by volume. For very accurate work, wash the combined oil layers with water until neutral. Drain the water off and determine the specific gravity of the oil, correcting to 15.56° C. (60° F.). If desired, a straight distillation can be made on the washed oil to obtain a more accurate distillation range.

Add hot dilute hydrochloric acid to the distillation flask and heat to boiling with vigorous shaking. Transfer the contents to a centrifuge bottle and wash the flask with hot water. Cool the flask and bottle and wash the flask thoroughly with ethyl ether, adding the washings to the centrifuge bottle. Proceed with the ether extraction as in the previous method. Wash the combined ether extracts with water until neutral. Evaporate the ether, place in the oven for the minimum time necessary to drive off all the ether, and weigh. This normally gives the fatty matter corresponding to the soap present in the sample, and a simple calculation gives the amount of soap. Melting point, if solid at room temperature, acid value, and iodine value identify the source of the fatty acid.

Wash the pigment or abrasive in the centrifuge bottle with water, again throw down with the centrifuge, and decant. Repeat this several times to remove the calcium chloride. Dry the residue *in situ*, brush out, and weigh. Identify by mesh analysis, microscopic examination, and, if necessary, by mineral analysis. The pigment or abrasive may also be obtained by ashing the original sample, if only a volatile soap is present.

Determine ammonia by distillation into standard acid. For this add water and calcium chloride, then sodium hydroxide solution, to the sample through a dropping funnel.

Subtract the amount of ammonia necessary to saponify the fatty acids from the total ammonia thus found, to give the free ammonia, if present.

Water-Base Wax Emulsions

This type of emulsion is of recent importance and generally consists of a wax, such as carnauba, together with a resin such as shellac, emulsified in water with the aid of soap. Ammonia and triethanolamine soaps are preferred, though alkali soap is sometimes used. Soda soap may cause the emulsion to become semi-solid in time. Borax is frequently present.

Since wax in substantial amounts is not completely soluble in ether, the procedures previously given cannot be used and it is necessary to work on the total solids of the sample. This is not a disadvantage in this case, as no oil is present and a constant weight is readily attained without altering the characteristics of the wax and resin.

Method. Extract 5 to 10 grams of the total solids with carbon tetrachloride for several hours, using a Soxhlet extractor. Little advantage is obtained by using the rubber extraction type of apparatus. Rapid refluxing keeps the carbon tetrachloride surrounding the thimble in the Soxhlet tube very little below its boiling point. Recover the solvent in an empty Soxhlet apparatus, take to dryness on a water bath and finally dry to constant weight in the oven at 110° C.. A fairly extended drying period is usually necessary.

Melting point, saponification value, and acid value determinations generally suffice to identify the wax. In case of doubt, iodine value, unsaponifiable matter, and aniline point will assist. Determine the unsaponifiable matter by saponifying 5 grams of an oil low in unsaponifiable matter, such as raw castor oil, with 0.5 gram of the wax dissolved in it and extract with ether in the usual way. Correct for the unsaponifiable matter in the oil used. Alternatively, saponify the wax directly with potassium hydroxide in carbitol (*6*).

The aniline point (*5*) is a recently developed constant which is particularly useful if a mixture of waxes is present, as is so often the case in commercial preparations. The determination is simple. Heat together 1 volume of wax, 1 volume of V. M. and P. naphtha, and 2 volumes of aniline in a test tube until a clear homogeneous liquid is obtained. Insert the test tube in an air bath and cool gradually by stirring with a thermometer. The aniline point is the temperature at which complete opacity of the liquid occurs, and is sharp and definite. Typical values are: carnauba wax 64°, beeswax 58.5°, paraffin (135° F. m. p.) 93.5°. Mixtures show values intermediate between those of the waxes present.

Extract the residue left in the thimble by carbon tetrachloride for several hours with hot alcohol in exactly the same way. Evaporate the alcohol. Analysis of this extract is not always simple. When alkali soap is present, titrate an aqueous aliquot, which is obtained by dissolving a weighed portion in alcohol and then diluting with a relatively large amount of water. This figure is not absolutely necessary but can be used as a check on the soap determined by titrating the ash of an original sample. Even this relatively quick method is not always simple, as borax is apt to be in the ash. Obtain the saponification value, acid value, and iodine value on the material extracted with alcohol to identify the resin present, if any. Test for rosin by the Liebermann-Storch reaction. As soap is present, it must be allowed for in interpreting the results.

The identification of the alcohol extract is further complicated when ammonia and triethanolamine soaps are present. These soaps, more particularly those of ammonia, decompose in the oven. The fatty acids so liberated are extracted by the carbon tetrachloride, and this must be borne in mind when dealing with the values obtained on the wax. The soap is usually present in relatively small amount compared to the wax and consequently the wax constants other than acid value are usually not greatly altered. The alcohol extract of samples containing ammonia, and to a certain extent triethanolamine, therefore

consists largely of the resin and identification is more definite. As the number of resins used commercially is very limited, identification is usually simple.

Determine ammonia on an original sample by distilling with sodium hydroxide after addition of calcium chloride to reduce foaming. The difference between the nitrogen due to the ammonia and the total nitrogen obtained by a Kjeldahl determination gives the nitrogen due to triethanolamine.

Obtain the borax on an original sample, preferably by the Ross-Deemer method. A quicker, though possibly less accurate method, is to titrate the carbonate and borax together on an ash of the original sample. Add glycerol and titrate the free boric acid with caustic soda. It is essential to boil off the liberated carbon dioxide after the total alkali titration. If alkali soaps are absent, the ash consists almost entirely of any borax present. Titrate directly with acid. There is always some extraneous ash from impurities in the commercial ingredients used, so that the weight of ash cannot be assumed to represent the borax content.

The methods given above have developed over a period of years and include suggestions from various staff members of Foster D. Snell, Inc., in particular from Cyril S. Kimball and Harry J. Hosking.

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An Electronic Bridge Balance Indicator for Conductance Measurements

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ELECTRON tube devices employed as alternating current bridge balance indicators have been described by Tulauskas (*8*), McNamara (*6*), and others (*1*). Tulauskas' device contains seven tubes and though McNamara's uses but two tubes, it has the disadvantage that the balance point is not indicated directly.

A single tube may be used to indicate the balance point of an alternating current bridge, as shown in Figure 1. The Type 75 tube functions first as an amplifier, then rectifies the alternating component of the plate current, and finally indicates on the meter in the plate circuit lead the magnitude of the impressed alternating voltage.

This arrangement is particularly efficient because the voltage from the bridge is first stepped up with transformer T_1, then applied to the grid of the tube, amplified, and again stepped up with transformer T_2. This amplified input voltage is now applied between diode and cathode through the high resistance, R_2. The rectified pulsating current flowing across R_2 produces a negative voltage which is converted to a direct current voltage by condenser C_1 and resistances R_1 and R_8. This direct current voltage is then applied to the grid and its magnitude indicated on the direct current 0–1 milliammeter in the plate circuit. Thus the tube functions simultaneously both as an alternating and direct current amplifier.

This arrangement is difficult to design, as degenerative or regenerative effects have to be avoided. In practice it is best to use transformer T_2 so that the voltage on the diode will be in phase with the alternating current voltage on the grid. The network R_3–R_4–R_5 is used to bias the diode as well as the triode and the values are chosen to bias the diode suitably, in order that it may be operated at the point of maximum curvature of the diode current–diode volts curve, thus insuring efficient rectification. A small steady or "null-point" input potential may be balanced out by reducing the negative bias on the grid, the latter being accomplished by adjustment of R_4, which has the effect of reducing the potential on the grid and diode simultaneously and in the same ratio.

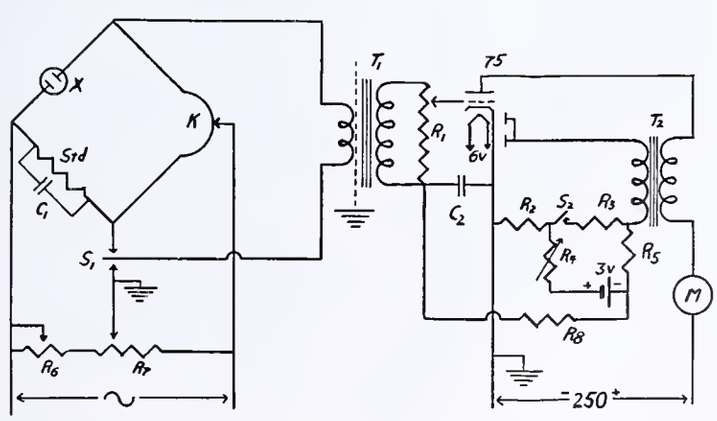

Figure 1. Diagram

R_1.	1 megohm volume control	T_2.	Interstage transformer
R_2, R_8.	1 megohm, 1 watt	C_2.	0.01 mfd. paper condenser
R_3, R_5.	10,000 ohms, 1 watt	S_1.	S. P. D. T. Yaxley jack switch
R_4.	75,000-ohm volume control	S_2.	S. P. S. T. switch on R_4
R_6.	5000-ohm volume control	K.	Kohlrausch slide wire
R_7.	100-ohm potentiometer	M.	0–1 milliammeter
T_1.	Input transformer		

This arrangement has an advantage in addition to its comparative simplicity, in that the meter reads maximum at zero impressed potential and the readings decrease as the potential is increased. Reasonable overloads normally encountered in bridge methods are therefore not harmful.

The sensitivity of this device is in the order of microvolts with a primary impedance of 100 ohms, which is probably comparable to that of untuned earphones. Since earphone ratings are not generally given because the sensitivity varies with the observer and the noise level in the laboratory, close comparison is not possible. Under ordinary laboratory conditions—that is, without sound-proof rooms—this single-tube device is more sensitive than earphones without a preamplifier and convenience of use is considerably greater.

Figure 2 is a plot of bridge setting against electronic indicator readings. The balance point can easily be located with an accuracy of 2 parts in 100,000, which corresponds to a resistance measurement with a precision of ±0.01 per cent and may be determined without graphing the results. With ordinary earphones under usual laboratory conditions the apparent dead silent region extends over practically the entire region shown in this plot.

Since the response of the human ear is logarithmic, precision measurement with the earphones requires a zero signal at

the balance point. This limitation does not apply to the electronic indicator, as residuals of a low order of magnitude may be compensated for by adjusting R_4, without any sacrifice in sensitivity. It must be remembered, however, that a faint note in the earphones corresponds to almost full scale on the indicator.

In any alternating current bridge earthing is important and too often neglected with resulting "head effect" and a minimum sound rather than silence at the balance point. Resistors R_6 and R_7 are the earthing network, a Wagner ground

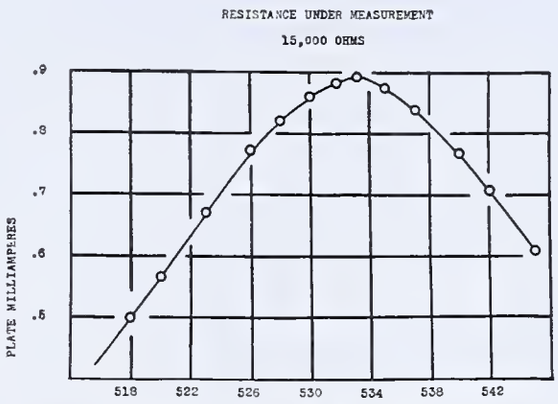

FIGURE 2. PLOT OF BRIDGE SETTING AGAINST ELECTRONIC INDICATOR READINGS

L. and N. Type K Kohlrausch slide wire with end coils.

(*9*) as used by Jones (*5*) and others (*7*). The single-pole double-throw switch offers a convenient way of adjusting the Wagner ground for each particular measurement. If the output transformer of the oscillator is not electrostatically symmetrical, precision measurements require the use of a variable condenser or inductor from ground to one of the output posts of the oscillator.

Condenser C_1 is necessary to compensate for the capacity effect of the conductance cell (*5*). Its importance is generally overestimated, for with a well-arranged bridge, proper treatment of the conductance cell, and the Wagner ground it can sometimes be omitted when only ordinary precision is required. When this is true, the effect of small phase angle shift can be compensated for by adjustment of resistor R_4.

The electronic indicator is connected to the bridge network through an impedance-matching transformer (*2, 3, 4*). While this transformer is necessary, its exact function is not widely understood. In this case its functions are, first, to isolate bridge and electronic indicator so that each may be properly grounded; second, to eliminate any possible electrostatic pick-up with the electrostatic shield of the transformer; and third, to provide a maximum transfer of energy from the bridge to the detector in order that the full sensitivity of the detector may be realized.

For maximum sensitivity the primary of this transformer should match the impedance of the bridge and the secondary should match the input impedance of the vacuum tube. The impedance of the bridge is, of course, variable and changes with the resistance under measurement. In practice, two arms of the bridge are usually a Kohlrausch slide wire, the resistance of which is comparatively low. As long as this is true, the slide wire becomes the deciding factor, so that to a first approximation the impedance of the primary should approximately equal the resistance of the slide wire and should be connected as shown in Figure 1. When the transformer is to be used with various slide wires, or with one slide wire with and without end coils, it should have a different primary winding for each, all electrostatically shielded from each other and from the secondary. The indicator may also be connected to the opposite side of the bridge by interchanging the oscillator and indicator. The Wagner ground must also be changed and the value of R_6 reduced to match the new bridge-arm ratio. Impedance-matching transformer T_1 should then be properly designed to match the bridge with this connection. In general, the bridge balance indicator may be used in any suitably arranged bridge as a substitute for the conventional amplifier and head phones. Several of these indicators have been in use in the authors' laboratory for the past year and the balance point has been compared repeatedly with that obtained with a preamplifier and earphones. With the precautions outlined the authors have never observed a discrepancy between the two balance points exceeding the experimental error.

With this electronic indicator measurements are not restricted to any one frequency. The response at any particular frequency depends largely upon the characteristics of the transformers used. Satisfactory measurements have been made as low as 10 cycles per second. The upper limit is about 10,000 cycles, but, of course, for precise work in this region the bridge must be designed for use at these frequencies.

The sensitivity of the device may be increased further by the addition of a high-gain tube as a preamplifier. Preamplifiers used in conjunction with earphones are usually tuned in order to suppress harmonics produced by the oscillator and to minimize the effects of tube noise. The noise level of tubes becomes the limiting factor for amplifiers and may easily be reached by two stages of high-gain amplification feeding a pair of phones. Since the noise level of tubes in a properly constructed amplifier is fairly constant and since it is possible to compensate for low alternating current inputs by adjusting R_4, preliminary experiments indicate that the lowest potential which may be detected with this arrangement is somewhat smaller than with the aural method.

Experiments on further details of this arrangement and others are in progress in the authors' laboratory.

Summary

A single tube may be used as a bridge balance indicator which in a suitable arrangement has a sensitivity equal to that of the best headphones. In using this electronic indicator to its best advantage, important factors are shielded impedance-matching transformers and proper earthing arrangement such as a Wagner ground.

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CORRECTION. In the article on "Colorimetric Methods for the Determination of Phosphorus" [IND. ENG. CHEM., Anal. Ed., 7, 228 (1935)] in paragraph 4 under the heading "Description of Methods," the second sentence should read "Exact quantity of MoO_3 in it should be known."

CH. ZINZADZE

Determination of the Alkali-Labile Value of Starches and Starch Products

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IN A PREVIOUS paper (*8*) it was shown that by measuring with hypoiodite the amount of material in a starch, amylose, or starch product that is attacked by hot aqueous alkali, a number could be obtained that was an index to the peculiar make-up of the sample in hand. Slight changes in the starch or starch product that cannot be detected by such well-known determinations as viscosity, specific rotation, color with iodine, and initial reducing value, are, however, immediately reflected in a change in the stability of the product to the action of hot aqueous alkali. While this has been used in a qualitative way (*3*) by others, the subsequent quantitative determination by iodometric titration of the extent of attack by the aqueous alkali has made the method of interest to starch chemists.

Every starch and starch product contains some material which is very quickly attacked by hot aqueous alkali and a part which is relatively slowly attacked by the same reagent. The latter part can be recovered substantially unchanged after the alkali has acted. The two parts have been called, respectively, alkali-labile and alkali-stable, the one being the antithesis of the other. Various pretreatments of the starches or their amyloses cause changes in the amount of this alkali-susceptible portion. By titrating iodometrically the alkali-digested solution of noncarbohydrate breakdown material having its origin in the alkali-labile portions, a number, expressed in milligrams of iodine per hundred milligrams of sample may be obtained. This is called the alkali-labile value.

A somewhat analogous procedure, called the copper-number determination (*2*), has been used to some extent in cellulose chemistry for a somewhat similar purpose. Both methods depend on reactions that have for their point of departure the attack of free or easily available aldehydic groups in certain parts or fractions of complex carbohydrates. The copper-number method is not, however, useful for application to the starches or starch products, one reason being that the hot aqueous alkali that causes the decomposition and the copper that measures it are both present during the operation. In the alkali-labile determination, on the other hand, the alkali is allowed to act, the solution is neutralized, and the effect of the hot aqueous alkali measured separately by hypoiodite solution, volumetrically. The small amount of cold aqueous alkali used in the iodometric determination produces itself no further alkali-labile material.

The method under discussion is a semi-micro one and very sensitive to changes in technic. After being applied to several thousand samples by several analysts, certain discrepancies in results made their appearance. Therefore all apparent variables were investigated one at a time and a modified method was evolved which, while giving slightly higher results than the older method, gives much greater precision. The values are still admittedly empiric, but with care and a little practice they can be duplicated and for comparative purposes serve very well.

Development of Method

The method may be divided into two parts—that which has to do with the hot alkaline digestion and subsequent partial or complete neutralization, and that which has to do with concentrations of iodine and alkali in the iodometric titration.

From experience the more important variables have been found to be:

PART I. (1) period of digestion in the hot 0.1 *M* alkali (This molarity was fixed when the original work was done. A departure from it will also cause a slight variation in samples of high alkali-labile value; otherwise there will be very little difference. The more dilute alkali gives the higher results during digestion.); (2) the elapsed time after digestion and before iodometric titration; and (3) the alkalinity or acidity during this period.

PART II. (1) period of contact with the hypoiodite solution before the thiosulfate titration; (2) amount of excess alkali present during treatment with iodine; and (3) amount of iodine in excess present during the hypoiodite treatment.

In these experiments a sample of dry cornstarch ground in a ball mill for 168 hours (*7*) was used as a standard. The iodometric titrations (*4*) were made at first by a slight modification of the Taylor and Salzmann (*8*) technic. In this first revision 5.00 cc. of 0.1 *M* alkali were added at one time and then enough iodine (as determined by a trial run) so that there would be about 0.75 cc. of iodine unused at the end of the operation. The values given in the first part of this paper are therefore on this basis. Subsequently it was found desirable, in the light of better understanding of the variables, to modify again this part of the analysis. The old and new values on this ground starch, however, bear a fixed relationship to one another, so any curves drawn with values for the former iodometric method will illustrate the argument but should not be taken as the best index values for a permanent record.

It became evident soon after the experiments were started that the alkali-labile values taken immediately at the end of the digestion in hot aqueous alkali were high but fell rapidly as the solution cooled, reaching an approximately steady state, the rate being dependent on the hydroxyl-ion concentration and the temperature while standing. The higher the alkalinity the shorter the time it takes for the solutions to reach a state of slow change at room temperature. If the alkaline-digestion mixture is chilled immediately after completion of the digestion and made acid, the high value may be fixed, so that the drift to a lower value is very slow. These results are shown graphically in Figure 1 where I shows drift in alkali-labile values in a solution neutralized to phenolphthalein (therefore still alkaline), III shows changes when excess acid was added after chilling immediately at end of digestion, and II after a sample was neutralized to phenolphthalein, allowed to undergo changes at this lower alkalinity for a time, and then over-acidified with hydrochloric acid and fixed at the lower value.

When the sample was left, on the other hand, in the concentrated alkali used in the digestion, the alkali-labile value dropped from 28.2 to 21.8 in 15 minutes at 25° C., but only to 23.0 in the same interval at 4° C. When kept at 25° C. for longer periods the alkali-labile value drifted slowly down, until at the end of a 6-hour interval it reached 17.0.

Because of the rapid drop in alkali-labile value in the early part of the interval after the hot aqueous alkaline digestion has been terminated by cooling, and even partial neutralization (to phenolphthalein), it is necessary, if the high initial value is to be preserved, not only to chill quickly but to make the mixture definitely acid. By adding excess acid immedi-

ately upon chilling the hot alkali-digested sample, the alkali-labile value is fixed and no longer drifts as it did when left on the alkaline side. While it is possible to over-acidify after a longer interval in the cooled alkaline mixture and stop the relatively rapid drift in alkali-labile values that in fact would go on even at phenolphthalein neutrality, these rather arbitrary values are not easily reproducible. Indeed, the

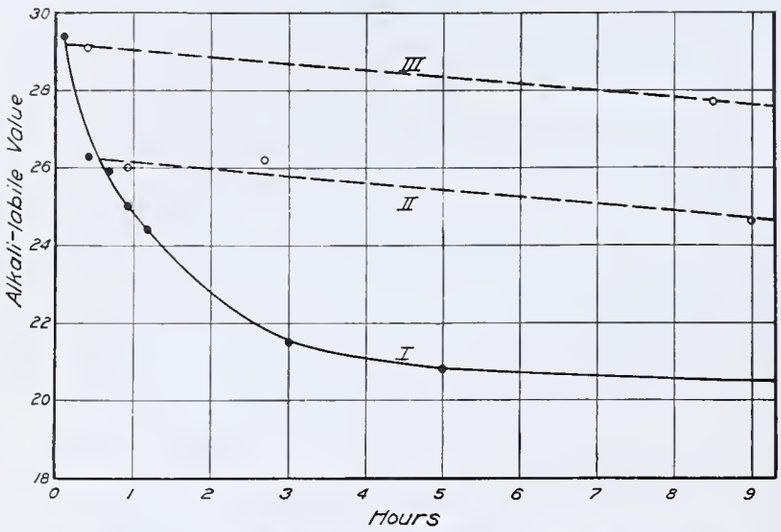

FIGURE 1. CHANGE OF ALKALI-LABILE VALUES WITH TIME, AFTER DIGESTION IN BOILING ALKALI

I. Solution neutralized only to phenolphthalein
II. Effect of excess acid in stopping change
III. Effect of excess acid added immediately to cooled digestion mixture

principal reason for lack of concordance among the results from various analysts is now easily explicable for, if the iodometric determination is made at different periods after the hot alkaline digestion, the values will be different and to a large extent a function of the personal habits of the analyst.

Except for this part of the determination, all other periods of treatment, concentration of reagents, and temperatures were selected so that the transformations involved at the particular points in the procedure had reached a steady state.

Turning to the cause for the drifting in alkali-labile value, it is probable that the behavior of the products from the alkaline decomposition of the carbohydrate material is due in part at least to aldol-type reactions which are known to be reversible with temperature in many cases (*5*) and catalyzed by hydroxyl ion. Apparently the materials when in equilibrium in the hot alkali may be kept approximately at that point by rapid chilling and slight over-acidification. Indeed, if the solution is made even slightly alkaline the alkali-labile values drift much more rapidly again to a new approximately steady state, temperature also having an influence.

If the determination must be interrupted, it is best to do this after cooling and quenching with acid after the digestion (Figure 1, III), for now the change is slow.

In the iodometric part of the determination, it was found that the amount of iodine in excess of that which will be used in the reaction does not affect the results as much as it was first thought to do. Keeping the amount of alkali used in the hypoiodite treatment constant at 5.00 cc. of 0.1 *M* sodium hydroxide but varying the amount of excess 0.025 *M* iodine solution, the alkali-labile value increases slowly and then decreases again. This is shown in Figure 2.

When, however, the amount of 0.025 *M* iodine is kept constant at 5.00 cc. and the amount of 0.1 *M* aqueous alkali is progressively increased, the alkali-labile values increase at a high rate. This is shown in Figure 3.

It is very important, therefore, to have the amount of alkali fixed at a known point before the sample is allowed to react with the iodine. (It should be borne in mind that aqueous alkali is used twice in the determination, once in excess at 100° C. for the digestion, and second in the iodometric determination to make hypoiodite. In the latter instance it is used, of course, in the cold and only in small amounts where its role is totally different from that in the first instance. Too large an excess of alkali converts all the iodine to iodate.) To this end the excess acid used in the first step to quench the alkali of the first hot digestion mixture is neutralized to some fixed point and an accurately measured amount of carefully standardized alkali added. Then the iodine is added as in the usual procedure and the mixture allowed to react.

Because phenolphthalein even in methyl alcohol uses iodine and because its turning point is back in the alkaline region where the solution begins to drift again, the new indicator nitrazine yellow (*9*) is employed (made by the Wenker Chemical Co., 616 Jackson Ave., Elizabeth, N. J.). This not only gives a sharper and more reproducible color change in the brown solutions but the change takes place very near pH7. Further, the indicator does not itself react with iodine. A careful back-titration of the excess acid with this indicator gives solutions which can be made uniformly properly alkaline for the subsequent iodometric technic.

The time interval of reaction with the alkaline hypoiodite also affects the results. As Figure 4 shows, the previously specified 15-minute period comes when the rate of change is high. Therefore a 45-minute interval was decided upon, for in this part of the curve the rate of change is very slow and the results therefore are easier of duplication with precision.

Below 20° C. the action of iodine and aqueous alkali (hypoiodite) on the digested samples proceeds so slowly that it has not reached a steady state at the end of 45 minutes. Concurrently iodate is formed in these solutions also and the active hypoiodite is removed thereby, so that the latter cannot function as it should with the decomposition products of the amylose. Between 25° and 30° C. under the conditions

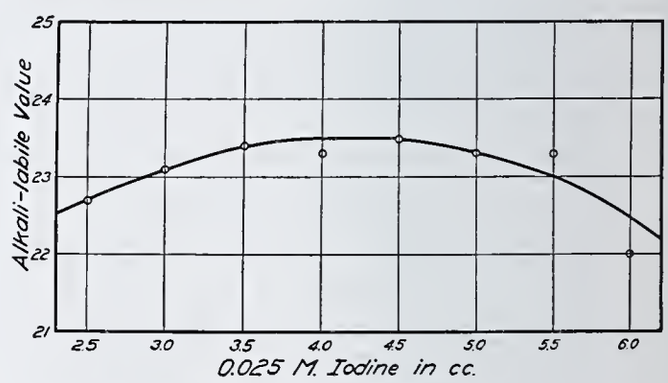

FIGURE 2. EFFECT ON ALKALI-LABILE VALUE OF VARIATION OF AMOUNT OF IODINE ADDED BEFORE BACK-TITRATION

Values represent excess of reagent over that consumed if the old method of digestion in the previous step is used. Relations are same in revised technic, but amounts of iodine are proportionately higher. In each case 5.00 cc. of 0.1 *M* alkali were added to form the hypoiodite.

given, the speed of reaction of the hypoiodite on the amylose decomposition products is much faster and in 45 minutes has reached a point beyond which there is substantially no change (Figure 4). During this time at the higher temperature the amount of iodate formed at the expense of the hypoiodite is apparently negligible and so does not affect the completeness of the reaction. The optimum conditions for the iodometric part of the determination were therefore set with these considerations in mind.

An iodometric method for determining reducing sugars has

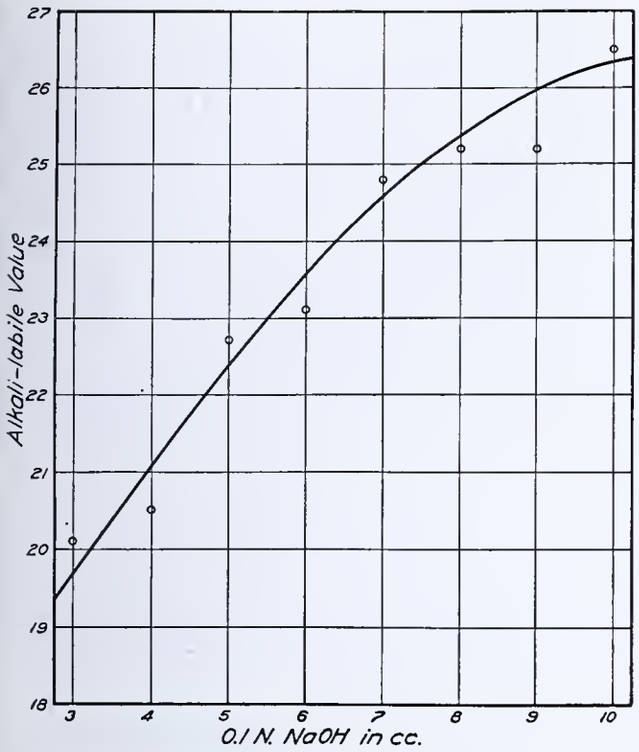

FIGURE 3. EFFECT ON ALKALI-LABILE VALUE OF VARIATION OF AMOUNT OF ALKALI PRESENT DURING TREATMENT OF DIGESTED MIXTURE WITH IODINE

In each case 5.00 cc. of 0.025 *M* were added.

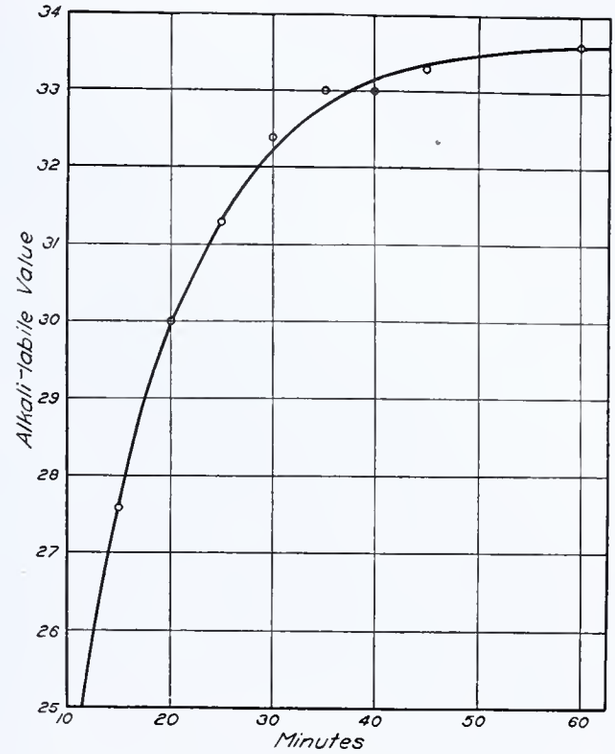

FIGURE 4. CHANGE IN ALKALI-LABILE VALUE WITH TIME INTERVAL DURING WHICH HYPOIODITE WAS ALLOWED TO ACT BEFORE BACK-TITRATION OF EXCESS IODINE WITH THIOSULFATE SOLUTION

been used in the past (*4*) and the iodometric part of this procedure is a modification of that original method. If the new adaptation is used to determine reducing value—that is, when the titration with hypoiodite is made without the preceding hot alkali digestion of glucose—the stoichiometric oxidation to gluconic acid is not complete. Were it complete, the reducing value in terms of milligrams of iodine per 100-mg. sample would be 141, whereas by this method it is 80 and the alkali-labile value at the end of 60 minutes is 66. In the last value the iodine consumed, of course, has reacted with the noncarbohydrate decomposition products, principally through the iodoform reaction. There is, therefore, no special significance to this so-called initial reducing value except in an empiric sense. Maltose monohydrate has an alkali-labile value of 67.1 (calculated anhydrous alkali-labile value of 70.7). It may be said, in general, however that for the amylose and dextrins the initial values are always much less than the alkali-labile values, while with glucose and maltose the initial values are always greater than the alkali-labile values, all determinations being made by the same iodometric procedure peculiar to the method.

A good grade of air-dried commercial cornstarch had an alkali-labile value of 22.8 and a commercial tapioca flour a value of 14.3. A certain thin-boiling starch, on the other hand, had a high characteristic value of 60, while several canary torrefaction dextrins had values at or near 20.

It is interesting to note that the initial reducing values expressed also in milligrams of iodine per 100-mg. sample of the three above-mentioned materials were substantially the same, about 9.0. These few data show the range of the alkali-labile values for widely differing products in contrast to the relatively constant initial values. Small amounts of glucose admixed with these starches and dextrins will contribute largely to the initial reducing value but hardly at all to the alkali-labile value.

The theoretical aspect of the alkali-labile value and its use in interpreting various transformations is the subject of work to be published in the near future.

On the starches the values by the new method are about 10 units higher than the old.

Procedure

The following solutions are required:

1. 0.1 *M* sodium hydroxide, slightly more than 4 grams per liter, diluted to proper molarity.
2. 0.1 *M* hydrochloric acid, 8.5 cc. of reagent hydrochloric acid made up to 1 liter with water.
3. Concentrated hydrochloric acid, reagent.
4. 0.025 *M* sodium thiosulfate, 6.2 grams of $Na_2S_2O_3.5H_2O$ made up to 1 liter with water (*1*).
5. 0.025 *M* iodine, 6.3 grams of iodine plus 35 grams of potassium iodide made up to 1 liter with water.
6. Phenolphthalein, 0.05 gram made up to 100 cc. of 50 per cent alcohol.
7. Nitrazine yellow, 0.1 gram made up to 100 cc. with water (*9*).

The absolute strength of iodine and thiosulfate need not be exactly 0.025 *M*, but should be standardized carefully (*1*).

The sodium hydroxide, however, should be accurately standardized at 0.1 *M* (within 3 to 5 parts per thousand) with potassium acid phthalate, using phenolphthalein indicator. The hydrochloric acid need not be standardized unless it is desired to know how much sodium hydroxide is used during the digestion.

PROCEDURE. It is convenient to run 12 determinations (6 samples) at a time. Each sample is run in duplicate.

1. Weigh approximately 50-mg. samples of the starch product into large Pyrex test tubes (20 × 2.5 cm., 8 × 1 inch). Weigh to 0.1 mg.
2. Add 10.00 cc. of exactly standardized 0.1 *M* sodium hydroxide to each test tube from a buret. The test tubes are loosely stoppered and floated in actively boiling water for 1 hour. Enough water should be used so that the tubes will float throughout the hour.
3. After the digestion, remove the test tubes from the bath, hold under running cold water for about 30 seconds, and then immediately acidify with 10 cc. of 0.1 *M* hydrochloric acid (use buret), with thorough shaking. It should not take over 1 minute from removal from bath to complete cooling and acidification.
4. Transfer the contents of the test tubes to 250-cc. Erlenmeyer flasks with two washings of 10 cc. each of distilled water. The time interval before the next step is not important. Two hours may elapse if necessary.

5. Add 2 drops of nitrazine yellow solution and neutralize with 0.1 *M* sodium hydroxide. Then add exactly (buret) 5 cc. excess of 0.1 *M* sodium hydroxide, and add immediately 5.00 cc. of 0.025 *M* standard iodine solution. It should not take longer than 2 to 3 minutes for neutralization, addition of excess alkali, and addition of iodine. Set in a dark place at 25° to 30° C. for 45 minutes. It is convenient to run the samples at intervals of 2.5 to 3 minutes as suitable to the individual analyst.

6. Forty-five minutes ± 1 minute after addition of iodine, add 5 cc. of concentrated hydrochloric acid, shake, then titrate immediately with 0.025 *M* thiosulfate. If the back-titer of thiosulfate is less than 3 cc., the resulting alkali-labile value will be low and 7 cc. instead of 5 cc. of iodine should be added for the oxidation of the next sample, so that the final back-titer is at least 3 cc. Some samples give a red color at the end point, so a little starch indicator has to be added; otherwise the stable amylose material left in the solution will act as the iodometric indicator without added starch paste.

Calculate the number of milligrams of iodine consumed, divide by the weight of the sample, and multiply by 100. The result is the alkali-labile value.

The average deviation among the results from several determinations on one sample will run ±0.5 alkali-labile unit, except when the sample is very nonuniform (some pastes) or in certain whole starches where gelatinization is slow and incomplete. Two operators making independent determinations will check to about 1.5 alkali-labile units. This should be considered satisfactory.

Pastes and other excessively wet samples may be treated with anhydrous, acetone-free methanol which when used in large quantities will precipitate out the solids. These can be dried and the alkali-labile value determined in the usual way. In samples low in electrolytes the alcohol will not bring about precipitation until a small amount of salt is added when there will be copious flocculation. For this purpose a few drops of 0.1 *M* barium chloride have been found to be most effective. Although better precipitants, such as acetone and ethyl alcohol, give more complete yields and do not cause fractionation of the amylose, they cannot be used because they consume iodine in the iodometric titration. Long drying in a vacuum oven will not remove the last traces of alcohol (*6*), so only methanol should be used. Starch as well as cellulose acts in this way.

Free chlorine, hypochlorites, peroxides, borax, and sulfur dioxide, as well as any other reagents that react with iodine or iodide ion, must be absent. However, the allowable limit of sulfur dioxide of 0.005 per cent is equivalent to only 0.02 alkali-labile value and may be neglected.

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Estimation of the Saccharifying Power of Malt Diastase

Adaptation of the Hagedorn and Jensen Method

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NO LINTNER method now exists which adequately fills the need for a short accurate process for the measurement of the saccharifying activity of diastase of plant origin suitable for general use in the analysis of malt, malt extracts, and similar products. Such a method should require only apparatus that is generally available in laboratories and should give concordant results in the hands of analysts working in different laboratories.

The classical Lintner method (*12*) needs no description here. While still retained as standard by English brewing chemists (*7*), it has been adversely criticized by Sherman (*15*) and by Browne (*2*), especially when applied to very active malts.

The Sykes and Mitchell method (*16*) is probably the most precise Lintner method when provided with pH control, but is too long for control purposes, especially as the filtration frequently is extremely slow. The operator has to contend with not only this delay, but, as has been noted by Hanes (*6*), with the possibility of back-oxidation of the reduced copper. Moreover, according to Blish (*1*), methods for estimation of reduced copper in Fehling's solution fail to give concordant results in the hands of collaborators in different laboratories.

The Sherman, Kendall, and Clark method (*15*) is one of the most accurate of those involving use of Fehling's solution. Its improved technic consists of adding the starch solution rapidly to the malt infusion, thus reducing initial timing errors to the minimum. Digestion takes place at 40° C. and a special scale has been developed for the expression of the diastatic activity. Like the Sykes and Mitchell method, however, it is too long for control purposes.

One of the standard methods used by English brewing chemists (*7*) is a form of the Lane-Eynon (*11*) method. This method is not sufficiently precise for application to highly active malts, and measurement of the initial reducing powers of the malt infusion and starch solution is difficult. Moreover, the Lane-Eynon method in general does not appear well suited for routine malt analysis because maltose acts upon Fehling's solution much more slowly than dextrose or levulose and it is necessary to boil for about 2 minutes after the addition of each portion of sugar solution before the full effect of the latter is manifest. The titration thus becomes decidedly cumbersome.

In the method of Windisch and Kolbach (*17*), adopted by continental brewing laboratories, the reducing substances formed in the substrate solution are oxidized by alkaline hypoiodate. The method as formulated is inadequate in dealing with highly active malts, while the hypoiodate technic as ordinarily used has been adversely criticized by Kline and Acree (*9*, *10*).

The polarimetric method (*3*) requires a special starch solution, and is operated at a higher concentration of substrate—nearly 5 per cent—than used in other Lintner methods. It

is the most rapid of all Lintner methods and substantially as accurate as methods involving the weighing of the copper oxide.

Hanes (*6*) described an exact titrimetric method for estimation of reducing substances formed by malt diastase, estimated as maltose, based on the Hagedorn and Jensen (*5*) micromethod for estimation of sugar in blood. For convenience and accuracy his method leaves little to be desired.

Blish and Sandstedt (*1*) likewise used the Hagedorn and Jensen method as the basis for an excellent method for estimating the reducing substances formed upon diastasis. Their method was applied to the study of saccharogenesis in flour suspensions. They discussed the results of the extended collaborative testing of the diastatic activity of flour, extending over a period of several years, and reported poor concordance of results when gravimetric copper reduction methods were used and when a picric acid method was tested. Excellent collaborative results were obtained, however, by using the principles of the Hagedorn and Jensen method.

They worked out and thoroughly tested complete specifications for a procedure based on the above method and adapted to the measurement of diastatic activity in flour suspensions. They found the method to be superior from the standpoint of accuracy, reliability, simplicity, and convenience to the technician, and expressed the opinion that "it should be conveniently possible to adapt the Hagedorn-Jensen method to advantage in the estimation of Lintner values." This suggestion has been carefully tested by the present authors, who find the procedure based upon the Hagedorn and Jensen technic superior to any existing Lintner method. It is fully as precise as the most exact of the maltose estimation methods, which use Fehling's solution, is shorter, and is far more convenient.

Because the Blish and Sandstedt modification permits larger amounts of maltose to be estimated than the Hanes method, the reagents specified by Blish and Sandstedt were selected as most readily adapted for the measurement of Lintner activity. It remained for the authors to work out the relationship of the reducing substances formed, estimated as maltose hydrate, to the alkaline ferricyanide consumed, and to fit the method to the analysis of malt and similar diastatic plant materials; since, as stated by Blish and Sandstedt, the table given by them is applicable only to solutions containing the special clarifying agents used in the measurement of diastasis in flour suspensions.

The method applied to the analysis of malt, described below, depends on the reduction of potassium ferricyanide in slightly alkaline solution, followed by acidification and titration of the ferricyanide remaining by standard thiosulfate.

Reagents

The following reagents are required, and are prepared according to the directions of Blish and Sandstedt (*1*):

Buffer Solution: Walpole's 4.6 acetate buffer consisting of a mixture of 102 cc. of *N* acetate acid and 98 cc. of *N* sodium acetate diluted to 1 liter.

0.4 *N* Sodium Hydroxide.

0.4 *N* Hydrochloric Acid.

Alkaline Ferricyanide Solution: 16.5 grams of pure dry potassium ferricyanide and 22 grams of anhydrous sodium carbonate, dissolved in water and diluted to 1 liter. This solution should be kept in a dark-colored bottle away from the light. The ferricyanide normality is 0.05.

0.05 *N* Sodium Thiosulfate Solution: 12.41 grams of sodium thiosulfate, dissolved in boiled-out distilled water and diluted to 1 liter. This solution may be checked against iodine solution which in turn is standardized against sodium arsenite, or the iodate titration method described by Hanes (*6*) may be used.

Acetic Acid Reagent: 200 cc. of glacial acetic acid, 70 grams of potassium chloride, and 20 grams of zinc sulfate ($ZnSO_4 \cdot 7H_2O$), dissolved in water and made up to 1 liter.

Potassium Iodide Solution: 50 grams of potassium iodide, dissolved in water and diluted to 100 cc. It contains 1 drop of concentrated sodium hydroxide to prevent deterioration on standing.

Soluble Starch Indicator Solution: 1 per cent solution of Lintner's soluble starch in 30 per cent salt solution. Suspend the soluble starch in water and pour into boiling hot water, cool, add the salt, and make up to volume. This solution keeps for several months.

Procedure

The 10-cc., 25-cc., and 50-cc. pipets should be calibrated, or, preferably, certified by the Bureau of Standards.

Preparation of Malt Infusion. Digest 25 grams of finely ground malt, prepared preferably by grinding 25 grams plus several extra kernels in a Seck mill, with 500 cc. of water at room temperature for 1.5 hours with occasional mixing. Filter, rejecting the first 50 cc. of filtrate.

Repeated tests on many different samples of malt by Steele show that the 1.5-hour digestion is amply long. The reason for the rejection of the first 50 cc. of filtrate is the known adsorption of malt diastase by filter paper, shown by Schultz and Landis (*14*). In case of malt sirups, mashes, etc., a multiple or fraction of a 5 per cent solution should be used, depending on the diastatic activity.

Preparation of Soluble Starch Solution. Heat about 750 cc. of distilled water nearly to boiling, add 22 grams of Lintner's soluble starch suspended in water, heat to boiling, cool, add 50 cc. of Walpole's 4.6 acetate buffer, and dilute to 1 liter at room temperature.

The starch used preferably should not contain more than 2 per cent of reducing substances estimated as maltose hydrate. Such starch can be readily prepared from high-grade potato starch, using the directions given by Lintner (*13*): The starch is mixed with 7.5 per cent hydrochloric acid and let stand for 6 days at 17° to 20° C. Then it is washed, suspended in water, and neutralized with a little sodium bicarbonate, thus neutralizing the last of the acid which clings persistently to the starch. It is then washed and dried in a gentle current of warm dry air.

The directions call for 22 grams per liter, so that when diluted by the addition of 10 per cent by volume of diastase infusion, the substrate concentration shall be 2 grams of air-dry starch per 100 cc., many tests having shown that more precise control of the starch concentration is unnecessary.

Digestion of Malt Infusion with Starch Solution. Dilute 25 cc. of the filtered infusion to 250 cc., transfer 10 cc. of the dilute infusion to a 200-cc. volumetric flask, and place in a water bath maintained at 20° C. At a noted time deliver 100 cc. of the starch solution also at 20° C. from a fast-delivery 100-cc. pipet, counting time from the moment when the starch solution reaches the infusion. At the end of 0.5 hour, add 20 cc. of 0.4 *N* sodium hydroxide from a pipet, mixing the first of the alkali instantly with the starch solution, thus abruptly checking the diastatic action. Neutralize the alkali by the addition of 20 cc. of 0.4 *N* hydrochloric acid, complete the volume to 200 cc., and mix well.

The sodium hydroxide used for terminating the diastatic action is neutralized with hydrochloric acid to prevent the possible injurious effect of the alkali on the oxidation of the reducing substances by the mild alkaline ferricyanide solution. The effect on the reaction of the salt formed was found to be negligible.

The increase in Lintner activity per 1° C. is about 8 per cent, so that it is necessary to keep the temperature at exactly 20° C., using a thermometer of known accuracy and graduated, preferably in tenths of a degree.

Titration. Transfer 25 cc. of the starch solution to a 500-cc. Erlenmeyer flask, and add 50 cc. of the alkaline ferricyanide. Mix well, and heat the flask and its contents for exactly 15 minutes in a boiling water bath, keeping the contents completely under the surface of the boiling water. Cool to room temperature, add 125 cc. of the acetic acid reagent and 5 cc. of the potassium iodide solution, and titrate with the standard 0.05 *N* thiosulfate.

Determination of Blank. Mix 10 cc. of the diluted infusion in a 200-cc. volumetric flask with 20 cc. of the 0.4 *N* sodium hydroxide. Then add 20 cc. of the 0.4 *N* hydrochloric acid and 100 cc. of the starch solution, dilute to 200 cc., mix, and measure the reducing power of a 25-cc. aliquot by mixing it in a 500-cc. Erlenmeyer flask with 50 cc. of the alkaline ferricyanide, heating, cooling, acidifying, and titrating as above described.

Evaluation. Calculate the net volume of 0.05 *N* ferricyanide consumed by subtracting the volume of 0.05 *N* thiosulfate required from the 0.05 *N* equivalent of the alkaline ferri-

cyanide solution, and correct by subtracting the 0.05 N ferricyanide value of the blank. Degrees Lintner are then computed by the formula $L = 8.092\ F$, where L is degrees Lintner and F is the net volume of 0.05 N ferricyanide consumed.

Table I shows analyses of a malt, a malt sirup of about 60 Lintner, and a malt sirup of about 300 Lintner.

Table I. Analyses

	Dilutions of 5% Infusion	0.05 N Thio-sulfate	0.05 N Ferri-cyanide	Net 0.05 N Ferri-cyanide[a]	Factor	Degrees Lintner
	Cc.	*Cc.*	*Cc.*	*Cc.*		
Malt	25 to 250	30.24	19.81	17.39	8.092	140.7
Blank	25 to 250	47.63	2.42	...	...	...
Malt sirup	50 to 250	29.4	20.65	13.90	8.092 × 0.5	56.2
Blank	50 to 250	43.2	6.85	...	...	...
Malt sirup	10 to 200	28.47	21.58	18.33	8.092 × 2	296.6
Blank	10 to 200	46.8	3.25	...	...	...

[a] Fifty cc. of the reputed 0.05 N alkaline ferricyanide were equivalent to 50.05 cc. of 0.05 N thiosulfate.

Titration

Hanes observed that the end point in the titration is extremely sharp. The authors find that the estimation of hundredths of a cubic centimeter can be approximated. The ratio of cubic centimeters of 0.05 N ferricyanide consumed to maltose oxidized was determined experimentally.

Fifteen minutes' heating in a boiling water bath was found to be preferable to 20 minutes' heating as recommended by Blish, who presumably worked at a slightly lower alkalinity.

The maltose hydrate used was recrystallized from alcohol and carefully dried. Its specific rotatory power (5 grams dissolved in water, heated to 90°, cooled, diluted to 100 cc. at 20° C., polarized at 20° C. at 37.7° V.) was $\alpha = 130.6$. A series of solutions was prepared in calibrated 200-cc. flasks and 25-cc. aliquots were mixed with 50-cc. portions of the alkaline 0.05 N ferricyanide solution, heated for 15 minutes in a boiling water bath, cooled, and titrated as above described, using Bureau of Standards calibrated pipets and buret.

Table II. Determination of Ratio

Maltose Hydrate	Alkaline 0.05 N Ferricyanide Reduced	Ratio of Maltose Hydrate to Ferricyanide Consumed
Mg./25 cc.	*Cc.*	*Mg./cc.*
25	13.06	1.91
50	26.64	1.88
75	39.57	1.89
87.5	46.0	1.90
		Av. 1.90

Evaluation

The evaluation formula is derived from the standard definition of the Lintner malt scale. Thus Browne (*2*) states, "a malt is given a diastatic value of 100 on Lintner's scale when 0.1 cc. of the filtered 5 per cent extract just reduces 5 cc. of Fehling's solution under the above conditions." In other words, a standard infusion of a malt of 100 Lintner is of such activity that 1 cc. of filtered extract corresponding to 50 mg. of sample produces sufficient reducing substances, reckoned as maltose hydrate, completely to reduce 50 cc. of Fehling's solution upon acting on a 2 per cent solution of soluble starch at 21° C. for 1 hour.

According to Browne (*2*) there are in 50 cc. Fehling's solution 438 mg. of copper, which are equivalent to 493.1 mg. Cu_2O. By extrapolation from the Munson and Walker table 493.1 mg. Cu_2O are equivalent to 408.3 mg. maltose hydrate. Thus, reducing substances consisting largely of maltose, equivalent in reducing power to 408.3 mg. of maltose hydrate, are formed under standard conditions by 50 mg. of malt of 100 Lintner.

In the above method 25 cc. of the digestion mixture correspond to 6.25 mg. of original sample. An infusion of 6.25 mg. of a malt of 100 Lintner acting on starch solution under standard conditions at 21° C. would produce 51.04 mg. of reducing substances per hour computed as maltose hydrate. If acting at 20° instead of 21° C., 6.25 mg. of a malt of 100 Lintner would produce only 92 per cent of the above amount of reducing substance, or 46.96 mg. per hour, equal to 23.48 mg. per half hour.

If we accept Kjeldahl's law of proportionality (*8*) as operative during the reaction, we may write the following formula $L = \frac{100\ m}{23.48}$, where L is the Lintner value of the malt and m is the amount in mg. of reducing substance reckoned as maltose hydrate. We can substitute for m its value 1.90 F where F equals cubic centimeters of alkaline 0.05 N ferricyanide reduced. We then have the expression $L = 8.092\ F$. The value 92 per cent is subject to revision, as it is only approximately correct. When redetermined, the value of the factor 8.092 probably will be slightly affected.

When we examine the classical papers of Lintner (*12*), we realize that the above definition of the Lintner scale can be accepted only if certain conventions are agreed upon. Thus Lintner seems to have specified room temperature only, and not 21° C. Again, while we may assume that he measured diastatic power within the optimum range (*4*) of its pH curve, we have no specific knowledge that this was done; indeed, he specified neutrality as the optimum reaction.

The writers believe that the Lintner activity should be considered to be a specific property of the diastatically active plant product as above defined. As a convenience the Lintner value may be measured at some other temperature (or pH) and the activity then calculated to true Lintner, provided that the temperature (or pH) coefficient is known.

In the method described above 20° C. is specified as the digestion temperature for greater convenience in malt analysis, since a water bath maintained at 20° C. is required in the estimation of extract.

Discussion

The above method introduces a technic of precision replacing methods based on Fehling's solution. It is offered tentatively for trial by those interested.

Acknowledgments

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Coal Carbonization—The Plastic Stage

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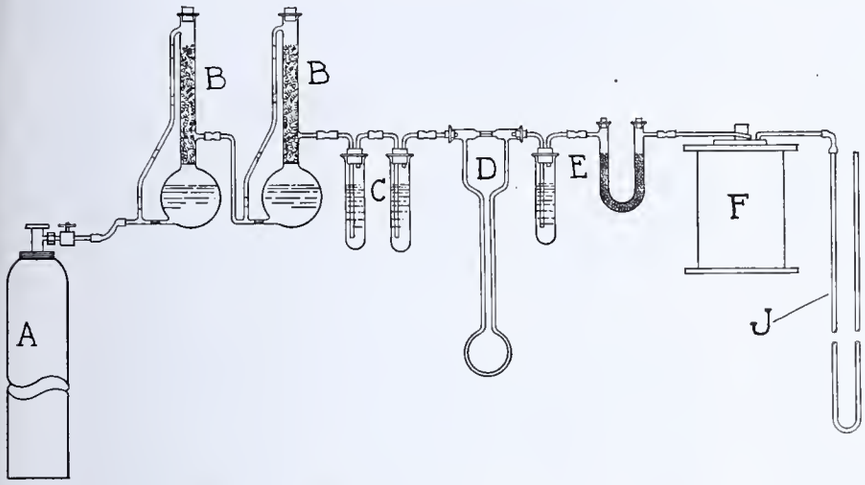

FIGURE 1. GENERAL ARRANGEMENT OF APPARATUS

A. Nitrogen cylinder
B. Oxygen removers
C. Wash bottles
D. Flowmeter
E. Driers
F. Coal fusion furnace
J. Manometer

IT IS WELL known that many bituminous coals soften when heated, presumably because of a fusion of some components of the coal and a fluxing of the more infusible parts by the fused material. The degree of plasticity reached varies greatly for different coals, in some cases there being only a mild sintering together of the individual particles, while in other cases the fusion is so complete that the individual particles disappear in the plastic mass of coal undergoing carbonization. If the degree of fusion is sufficient to close the interstices between coal particles, the gas being generated by the decomposing coal causes the mass to swell and become spongy. As carbonization proceeds, the plasticity grows less and eventually a cellular coke is formed.

Of the methods for studying the plastic stage in coal carbonization, the gas-flow test devised by Foxwell (*5*) has been widely used. Foxwell placed a small charge of crushed coal in a horizontal tube electrically heated. An inert gas was passed slowly through the tube as the temperature was raised, and the resistance of the coal charge to the gas flow was measured. As the coal softened, the gas pressure required to maintain constant gas flow increased to a maximum and then decreased to nearly its initial value. A curve with resistance to gas flow as ordinates and temperatures as abscissas was then plotted for each coal. Foxwell evidently believed that the temperature at the beginning of the resistance increase marked the beginning of the plastic condition and that the temperature when the resistance to gas flow had again fallen to its initial value marked the end of the plastic condition of the coal. He regarded the magnitude of the maximum resistance and the area under the resistance-temperature curve as criteria of the degree of plasticity of the coal. It will be shown in the present paper that some of these conclusions are in error.

Layng and his associates (*6, 7, 8*) used a modified Foxwell apparatus. They believed that the plastic temperature range lay between the points of initial pressure increase and maximum pressure, and they attached importance to the slope of the gas pressure–temperature curve between these points. These conclusions are also in error.

Lloyd (*9*) maintained approximately constant gas pressure in his apparatus and measured the decrease in the rate of gas flow as the coal softened. He believed that he was able to correlate the rate of flow–temperature curve with the coking characteristics of the coal. Ball and Curtis (*1*) greatly improved the Foxwell apparatus and used it in measuring the initial temperature of softening of various coals, but did not attempt to interpret the pressure-temperature curves obtained.

Recently Bunte and Lohr (*2, 3*) have reported a study of the plastic state by the Layng-Hathorne apparatus. Great importance was ascribed to the change of slope of the gas pressure–temperature curve.

In view of the conflicting opinions as to the correlation of the gas pressure–temperature curve obtained in the Foxwell procedure with the condition of the coal during carbonization, the present authors undertook, first, a study of the factors influencing the results, and subsequently, a correlation of the pressure-temperature data with data on plasticity obtained by another method.

Apparatus Used

The general arrangement of apparatus used for studying the influence of various factors in the Foxwell method is shown in Figure 1. Figure 2 shows the details of the furnace, which was essentially the same as the Ball and Curtis apparatus, except that the gas pressure was measured in the space below the coal charge instead of in the steel tube bringing the nitrogen to the apparatus.

The nitrogen was drawn at constant rate from a high-pressure commercial cylinder of the gas. It was passed through an oxygen-

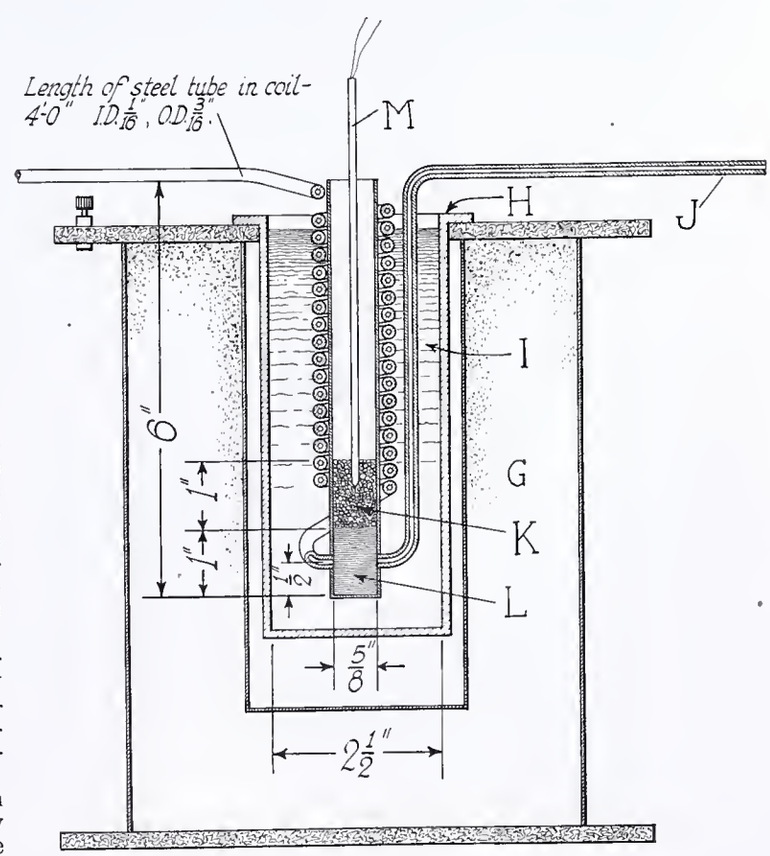

FIGURE 2. COAL FUSION FURNACE

G. Electric furnace
H. Iron container for lead bath
I. Lead
J. Manometer
K. Coal charge
L. Copper wool support for coal charge
M. Thermocouple

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[2] Present address, Tennessee Valley Authority, Knoxville, Tenn.

absorption apparatus (*11*) using reduced ammoniacal cuprous chloride, then through sulfuric acid wash bottles, through an orifice flowmeter and a bubbling tube, and finally through a drying tube containing calcium chloride. The purified, dry nitrogen was then passed through the apparatus shown in Figure 2, and the gas pressure–temperature curve determined—i. e., gas pressure readings on the manometer, *J*, versus temperature of the coal charge, as measured by the thermocouple, *M*.

Variables in the Foxwell Procedure

With a given apparatus and a given coal, the variables which most influence the results obtained are presumably the following: rate of gas flow through the coal charge, packing of the crushed coal in the fusion tube, length of the coal charge in the fusion tube, screen analysis of the coal used, and rate of heating of the coal as softening point is approached and during the plastic stage.

It will be noted on referring to the previous articles on the Foxwell method that the values selected for the above variables differed widely. Rates of gas flow were in the range 10 cc. per minute per square centimeter cross section of fusion tube, up to 177.3 cc., and in some cases were not held constant during the run; little attention was paid to the packing of the coal charge; the length of coal charge was in the range 2.5 to 10 cm.; the screen analyses were different and in some cases all the coal sample was used, whereas in other cases the finer screen sizes were rejected; and the rates of heating used by various investigators were in the range 1° to 5° C. per minute. If comparisons are to be made of the results obtained by different investigators, it is necessary to know the extent to which changes in the values of the variables altered the results. It will also be desirable to standardize the apparatus

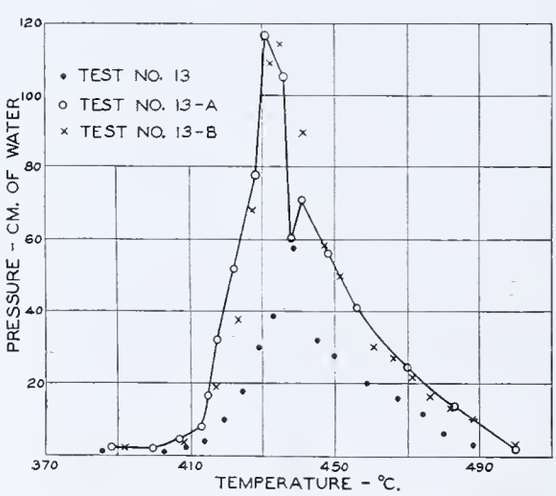

FIGURE 3. TEMPERATURE–GAS PRESSURE DATA FROM TRIPLICATE RUNS

itself if it is to be continued in use, for it appears fairly obvious from a study of the arrangements of parts adopted by the several investigators that the temperatures recorded were not in all cases those of the coal charge.

In the present work, the apparatus adopted was one which Ball and Curtis had shown to be reasonably satisfactory. It was necessary to adopt a set of values for the factors listed above, and to keep all these the same from run to run except only the factor purposely changed to study its influence on the gas pressure–temperature curve. After a considerable amount of preliminary work in adjusting the various factors to give smooth operation of the apparatus, the following were adopted as tentative standard values:

Rate of gas flow: 6 cc. per minute per sq. cm. cross section of fusion tube
Packing: as described below
Length of charge: 2.5 cm. (4.3 grams of coal)
Screen size of coal: all pass 10-mesh, not more than 25 per cent 80-mesh
Rate of heating: rapidly to within 10° to 20° of the softening temperature, thereafter at 2° C. per minute

In the study of the effects of the factors in the gas-flow test, a single coal of medium volatile matter content and normal plastic characteristics was used in all determinations.

Effect of Rate of Gas Flow

With conditions "standard" as specified above, and using the same medium volatile coal in successive tests, the rate of gas flow through the coal charge was varied from 2.9 to 12 cc. per minute per square centimeter cross section of tube, with results shown in Table I.

TABLE I. EFFECT OF VARYING RATE OF GAS FLOW

Test No.	Rate of Gas Flow	Temp. of Initial Fusion	Temp. at Max. Pressure	Max. Pressure	Remarks
	Cc./min./sq. cm.	*° C.*	*° C.*	*Cm. H_2O*	
11	2.9	405	445	19.0	Note large variations in maximum pressure in duplicate runs
11-A	2.9	400	445	67.6	
11-B	2.9	405	445	57.7	
11-C	2.9	405	445	73.0	
12	4.4	405	440	77.0	
10	6.0	400	440	83.0	
14	9.3	400	430	72.0	
13	12.0	400	440	58.8	Same remark as above
13-A	12.0	395	430	117.0	
13-B	12.0	400	435	114.0	

It will be observed in Table I that neither the temperature of initial softening (first increase in pressure) nor the temperature of maximum resistance to gas flow is changed notably by a fourfold increase in rate of gas flow. A rate of 6 cc. per minute per square centimeter cross section was retained as a standard rate for further work. From the known facts regarding coal carbonization it is probable that a very high rate of gas flow would change the observed temperatures.

The maximum gas pressure reached varied widely, even for the same rate of gas flow in successive experiments. These conclusions are similar to observations of Bunte and Lohr (*2*, *3*).

As an indication of the type of gas pressure–temperature curves obtained, the data for triplicate tests 13, 13-A, and 13-B are shown in Figure 3. It will be noted that the temperature at which softening of the coal begins is fairly reproducible, but there is considerable variation in the maximum gas pressure reached and in area under the curve. Additional evidence as to the lack of reproducibility in the values of the maximum gas pressures is found in the quadruplicate tests, 11, 11-A, 11-B, and 11-C in Table I.

Effect of Packing the Coal Charge

It would appear desirable in a procedure of the kind under study to have the coal charge uniformly packed from test to test. The resistance offered to gas flow at a constant rate through the coal charge was used as a criterion in determining which of several methods gave the most reproducible packing. It was found that the following relatively simple procedure gave a closely reproducible packing of the charge and was adopted as standard:

The stock sample was thoroughly mixed and then approximately 1-gram portions of coal were added to the fusion tube, the tube being gently tapped meanwhile. After each 1-gram addition the surface of the coal in the tube was leveled to prevent sizing of later additions through rolling of larger particles to the wall of the tube.

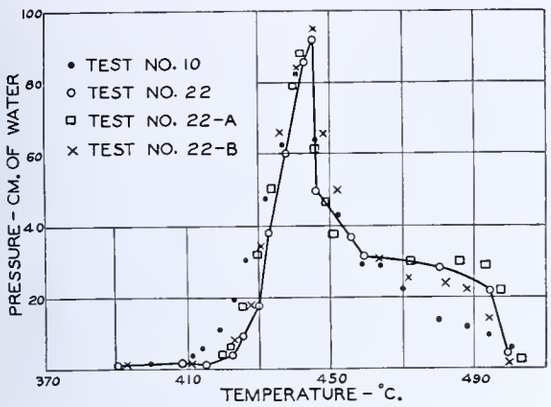

FIGURE 4. TEMPERATURE–GAS PRESSURE DATA

From runs 10, 22, 22-A, and 22-B, showing effect of eliminating fines from coal charge

In order to determine whether the density of packing had any effect on the pressure-temperature curves obtained, three runs were made with charges in which the density of packing had been increased by prolonged tapping of the tube. The temperatures of initial fusion and the temperature at maximum pressure were not changed; the maximum values reached by the gas pressure were somewhat increased, but these pressures are variable even under the most constant conditions which could be set up.

Effect of Length of Coal Charge

Duplicate tests were made with charges of lengths 2.5 cm. (4.3 grams), 3.8 cm. (6.5 grams), and 5.0 cm. (8.6 grams). In all cases the temperatures of initial fusion checked those of Table I within experimental error. Likewise the temperature at maximum gas pressure was the same for the 2.5-cm. and the 3.8-cm. charges. The 5.0-cm. charge swelled so much as to overflow the fusion tube and lift the thermocouple, so that no significant reading of temperature was had. In view of the above results a standard charge of 2.5 cm. (4.3 grams) was retained as specified in the table of tentative standard values.

Screen Analysis of Coal Charge

It was early found that the results of the Foxwell procedure were influenced considerably by the screen analysis of the coal charge. Some of the investigators cited above rejected the finer sizes. For many coals this rejection of the particles below, say, 80-mesh may not change the results, but the fact that most bituminous coals are made up of layers of unequal hardness, and actually show more or less concentration of the component parts in the various screen sizes, makes it appear obvious that all the screen sizes in a given sample should be used.

The standard sample of coal used in the present study of the variables of the Foxwell procedure was a coal (No. 56) from the Lower Kittanning seam, of the following proximate analysis: volatile combustible matter 22.3 per cent; fixed carbon 73.0 per cent; ash 4.7 per cent. It was ground to the following screen analysis:

Cumulative Per Cent through Tyler Standard Screen Sizes

Screen	10	20	28	48	80	100
Per cent through	100	77.2	61.7	36.2	22.9	17.2

Test 10 (Figure 4) was made with this standard sample. In tests 22, 22-A, and 22-B, also shown on Figure 4, all the coal passing a 50-mesh screen (30.6 per cent) was rejected in making up the coal charge. The comparison of these three with test 10 gives the effect of eliminating the fines—i. e., a slight increase in the temperatures of initial softening. The small variation in the magnitude of maximum pressure in the triplicate tests 22, 22-A, and 22-B, as compared with the wide variations shown in Figure 3, should be noted and explains, possibly, why previous investigators who eliminated fines were able to obtain reasonably reproducible results in respect to maximum pressures reached.

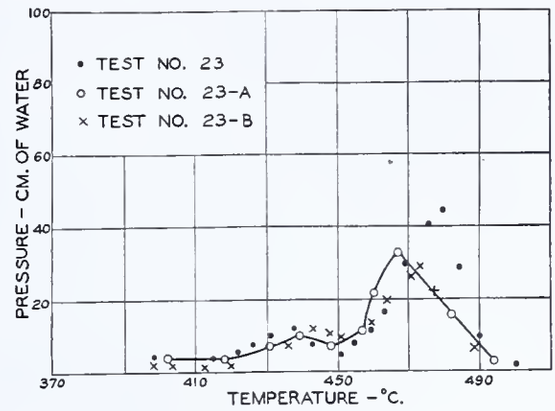

FIGURE 5. TEMPERATURE–GAS PRESSURE DATA

From runs 23, 23-A, and 23-B, showing results with fine coal present

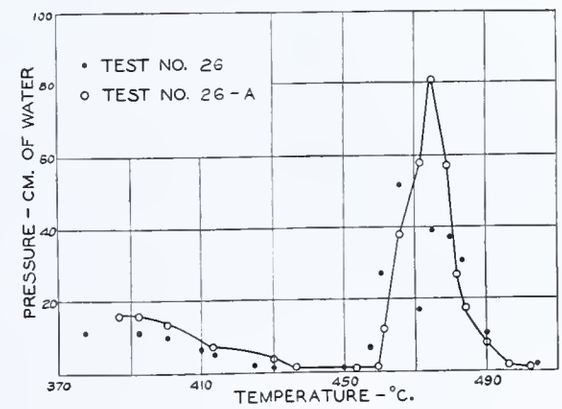

FIGURE 6. TEMPERATURE–GAS PRESSURE DATA

From runs 26 and 26-A, with coal ground to pass 80-mesh screen

The standard coal sample was next reground to the following screen sizes:

Cumulative Per Cent through Tyler Standard Screen Sizes

Screen	10	20	28	48	80	100
Per cent through	100	99.2	97.9	74.3	46.0	36.0

With this finer ground sample tests 23, 23-A, and 23-B (Figure 5) were made. The temperature of initial softening was increased somewhat for two of the three tests. The gas pressure–temperature curve in all three tests passed through a first maximum in the temperature range 435° to 445° C., but rose again in all cases and passed through a second maximum in the temperature range 465° to 480° C. The amount of finely ground coal present evidently influenced the results considerably.

The standard sample was next ground so that all would pass 80-mesh and tests 26 and 26-A (Figure 6) were made with this fine material. The gas pressure–temperature curves in these tests were different from any of the previous ones. At about 390° C. in both cases the pressure began to decrease until in both cases a temperature of about 450° to 460° C. was reached. The curves then rose sharply to maxima in the temperature range 465° to 475° C. The large influence of the fine material was again apparent.

Realizing that the large influence of screen analysis of the coal charge would be a serious deterrent toward standardizing the Foxwell procedure, an attempt was made to avoid the difficulty. The coal sample was first ground to pass 150-mesh,

then moistened with 10 per cent of water and briquetted without binder, the briquet being then crushed and ground, and the ground material separated into various screen sizes. This procedure presumably gave a product of the same composition in all the screen sizes, so that, by reblending the fractions in suitable proportions, any desired standard screen analysis could be obtained. In test 24, the sample was made up in this manner with a screen analysis approximately the same as that of the standard sample used in test 10. In test 25,

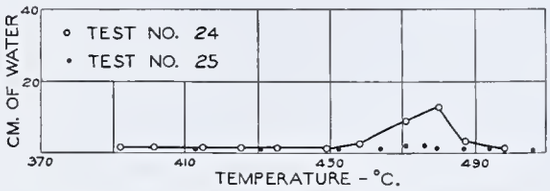

FIGURE 7. TEMPERATURE–GAS PRESSURE DATA

From runs 24 and 25, showing effect of fine grinding, briquetting, and recrushing coal

a blend was made of the −20 to +28-mesh fractions of the ground, briquetted, and reground coal. The temperature-pressure data obtained with these two samples are shown in Figure 7 and are entirely different from those of the standard sample (test 10). The fusing characteristic of the coal had been almost destroyed. One thinks immediately of oxidation, since it is well known that oxidation does decrease the degree of fusibility of coal. The coal used, however, was a high-rank coal in which oxidation proceeds slowly. Moreover, no oxidation effect was noted in the other finely ground samples. From the shape of the plastic curve it would appear that raising the temperature of the coarse particles caused them to disintegrate and, consequently, the charge finally consisted of very fine particles when the plastic range was reached. The two experiments showed that the difficulty of duplicating screen analyses in the Foxwell method could not be avoided by grinding, briquetting, and regrinding, logical as this procedure may seem.

The large influence of screen analysis of the coal charge raised what appears to be a serious difficulty. If, however, a given coal be ground to pass 10-mesh and the amount passing 80-mesh be kept below 25 per cent by suitable grinding, the Foxwell procedure gives fairly consistent values for the temperatures of initial softening and the temperature of maximum gas pressure.

Effect of Rate of Heating

From the known behavior of coal during carbonization, one would anticipate that either a very slow or a very rapid rate of heating would tend to increase the observed temperature of initial softening. At a very slow rate fused material accumulates more slowly, whereas at a high rate of heating the relatively slow coal decomposition processes, which give rise to fused material, cause a lag between the time the coal reaches the necessary temperature for softening and the time when the gas passages through the coal charge close sufficiently to show increased pressure in the apparatus. Foxwell, and later Davidson, found rate of heating, within the range they used, to be without appreciable effect on the temperature of initial softening. Ball and Curtis observed, however, a small increase in softening temperature when the rate of heating was increased from 2° to 5° C. and to 8° C., while at 0.5° C. per minute the coal became nonfusing. It was observed in the present work that between rates of 1° and 4° C. per minute there is only a small tendency to obtain higher temperatures of initial softening and of maximum pressure with the higher rates of heating. A rate of 2° C. per minute was retained as a standard.

Standardization of Foxwell Procedure

The temperature which can be most certainly determined in the Foxwell procedure is that at which the coal softens sufficiently to begin to close the gas passages through the charge of crushed coal. With an apparatus such as shown in Figures 1 and 2, using purified nitrogen, and the standard conditions outlined above, this temperature may be determined within about 5° C. in successive runs.

Having adopted some suitable set of standard conditions, such as given above, it will be found that the observed temperature of initial softening of the coal is not appreciably affected by small changes in rate of gas flow, in length of coal charge, in rate of heating, or in method of placing the coal charge in the vertical fusion tube. The rather large effect of the screen sizes of the coal charge raises the main difficulty, but if the coal be ground to pass 10-mesh and the fines (below 80-mesh) be kept less than 25 per cent, duplicate runs on the same coal will give about the same observed initial softening temperature.

The temperature at which the gas pressure ahead of the coal charge reaches a maximum cannot be determined as certainly as can the temperature of initial softening of the coal, but a consideration of all the data on tests mentioned above indicates that this temperature is probably also a characteristic of the coal, although not so well defined, and of less certain significance in the carbonization process.

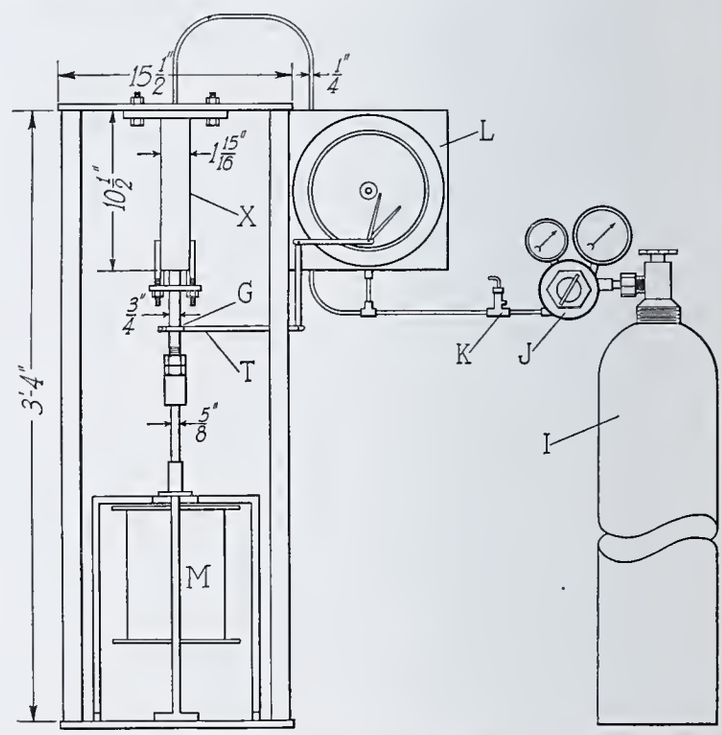

FIGURE 8. EXTRUSIVITY APPARATUS

Not drawn to scale

G.	Piston	*L.*	Recorder
I.	Compressed air	*M.*	Extrusion apparatus
J.	Pressure-reducing valve	*T.*	Lever system
K.	Vent valve	*X.*	Cylinder

The maximum gas pressure varies in successive runs, in spite of attempts to keep all conditions the same. It is obvious that the slope of the gas pressure–temperature curve, to which Layng and his associates attempted to give significance, will depend on a number of factors, such as (1) rate of gas delivered to the apparatus compared with volume of the gas purification train, tubing, etc., ahead of the coal charge, (2) rate of closing of the gas passages in the coal charge (3) rate of heating of that part of the gas which is passing through the heating coil in the lead bath, etc. Even with conditions as nearly the same as may be in duplicate runs, the

magnitude of the pressure developed seems to be determined by a fortuitous combination of events in the coal. The slope of the gas pressure–temperature curve has evidently no such significance as given in some of the papers of Layng and his associates, nor is the area under the pressure-temperature curve or the maximum pressure developed a characteristic of the coal.

During the present investigation, evidence was secured showing that the height of the gas pressure–temperature curve as a measure of the degree of plasticity reached by a coal during carbonization was not in agreement with the degree of plasticity as indicated by the amount of swelling observed when small briquets of the coal were carbonized.

Condition of Coal While Taking Pressure-Temperature Data

The initial increase in gas pressure observed in the pressure-temperature curve is certainly had when the coal has softened so that it begins to flow under its own weight and thus closes the gas passages through the charge. It has been shown by Ball and Curtis (*1*) that coal is somewhat plastic at temperatures considerably below the so-called "softening point" as determined by the Foxwell method. It appears, however, that the increase of plasticity with temperature increase is high in the neighborhood of this softening point and that the temperature of the softening point so determined is truly a characteristic of the coal.

The condition of the coal during the balance of the period during which the gas pressure–temperature data are taken in the Foxwell method is by no means so evident. The divergent views on this point have already been noted. Inasmuch as Layng assumed that the maximum in the gas pressure–temperature curve obtained in the Foxwell procedure marked the temperature at which the coal ceased to be plastic, this point was subjected to direct observation in an apparatus described below. It was easily shown that the coal charge was plastic at temperatures above that of maximum gas pressure observed in the gas-flow procedure, and that Layng's conclusion was therefore in error.

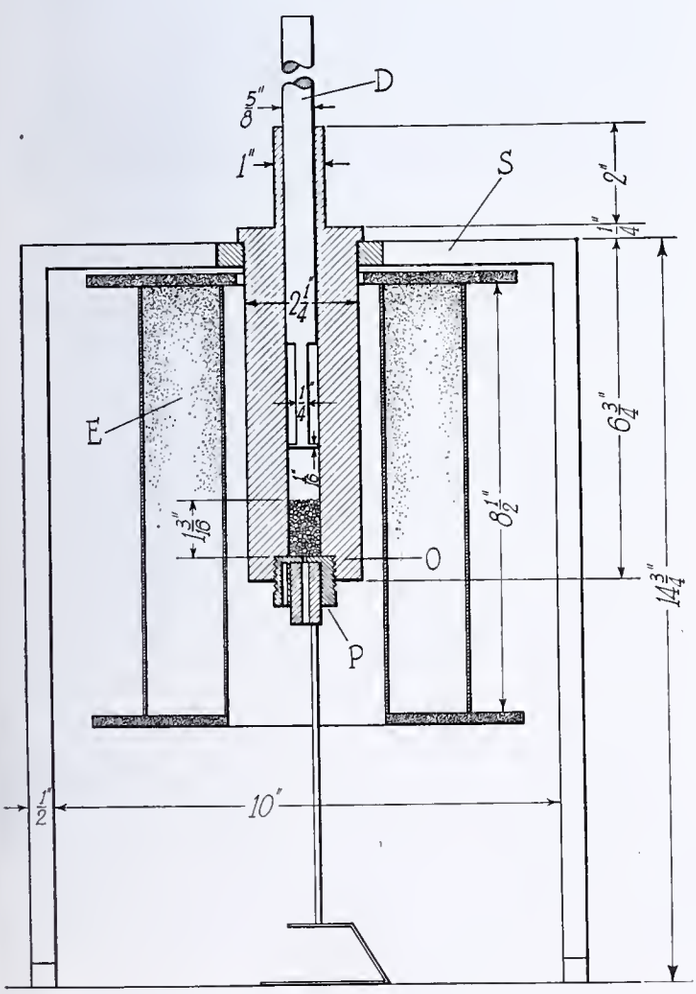

FIGURE 9. EXTRUSION CYLINDER

D. Plunger
E. Electric furnace
O. Steel cylinder
P. Orifice fitting
S. Supporting frame for cylinder *O*

Extrusivity of Coals in Plastic Condition

In order to secure further information as to the condition of a "fusing" coal in the temperature range above the softening point, and also in the hope that a test procedure might be developed which would give additional data serving to characterize coals, attention was turned to measurement of what may be termed the "extrusivity" of coals in the plastic condition.

Briefly, this term is used to express the rate at which coal in the plastic state may be extruded through an orifice or short tube under fairly closely controlled conditions of temperature and pressure in a given apparatus. It was recognized, of course, that the term "extrusivity" as here applied could not be given any such respectable scientific standing as adheres to the term "viscosity" (quite aside from the violence done etymology in coining the term "extrusivity"). Coal in the so-called plastic condition is not strictly a homogeneous body; it is at the time undergoing chemical changes and concomitant physical changes; it is liberating gases and vapors. Any attempt to measure a rheologic property of such a material must appear bizarre. Whether or not the conditions could be controlled sufficiently and the inevitable causes of inaccuracy reduced to a point where measurements characteristic of the coal could be made was the question to be answered. Porter (*10*) has published some data bearing on this problem.

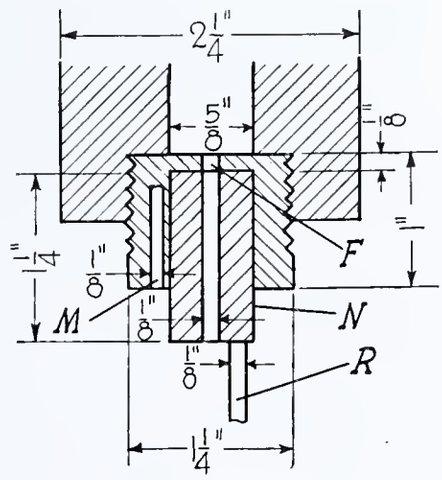

FIGURE 10. ORIFICE FITTING

F. Orifice proper
M. Thermocouple well
N. Plug
R. Spring support for plug

Apparatus for Measuring Extrusivity

The apparatus is shown diagrammatically (not to scale) in Figure 8.

Gas from high-pressure cylinder *I* was passed through pressure-reducing valve *J*, through vent valve *K*, and used in cylinder *X* to operate a piston, *G*, whose position was recorded continuously through the lever system, *T*, on the recorder, *L*. The pressure in the gas line was also recorded continuously on *L*. The motion of piston *G* was transmitted to the plunger in the extrusion apparatus, *M*, shown in detail in Figure 9. In this apparatus steel cylinder *O* received plunger *D*. The lower end of the plunger rested on the coal charge. The plunger was cut away a short distance from the lower end to provide a space in which any small amount of plastic coal which pushed past the head of the plunger would be caught. The steel cylinder, *O*, was surrounded by an electrically heated furnace, *E*, and was supported independent of the furnace by the frame, *S*. The lower end of the steel cylinder carried a steel orifice, *P*, shown in cross section in Figure 10. The orifice proper is shown at *F* in Figure 10 and had a thickness of 0.318 cm. (0.125 inch).

The following sizes of orifices were used:

Orifice No.	Diameter	
	Cm.	*Inch*
3	0.795	0.313
4	0.397	0.156
5	0.238	0.0938

The orifice body was drilled to receive a thermocouple at *M*. The plug, *N*, served to hold the coal in place while it was being heated preliminary to extrusion, during which period a thermocouple was kept in the coal charge through the hole drilled in the plug. The plug was held in place by the spring support, *R*.

During extrusion a beam of light was thrown on the orifice and the extrusion process observed in a suitably placed mirror.

The pressure recorder was calibrated and from time to time during the experiments the pressure necessary to overcome the friction between the moving piston and the packing in cylinder *X* was measured. This value and the weight of the piston were used to obtain the actual pressure applied to the coal charge from the pressure indicated on the recorder.

Five grams of coal were taken for each test and placed in the apparatus as shown in Figure 9. The temperature of the coal was then raised nearly to that desired, the plunger inserted, plug *N* removed, and the fusion tube and furnace were moved quickly into place as shown in Figure 8. Pressure in air cylinder *X* had meanwhile been brought to the desired value, movement of the piston being prevented mechanically until the extrusion apparatus was in place.

As soon as pressure had been applied to the coal, the orifice was observed. When extrusion began, electrically driven recorder *L* was started, giving a continuous record of time, gas pressure in cylinder *X*, and movement of piston *G*.

In all work with such a material as coal, there is difficulty in determining the temperature of a sample at any moment, and for this reason much of the published research on coal does not correctly correlate the actual temperature of the coal with other recorded observations. In the present work it was not possible to measure accurately the temperature of the coal at the moment of extrusion, but a fairly close approximation was made in the following manner: With plug *N* in place, a thermocouple was passed through the hole in the plug into the coal charge for a distance of 0.635 cm. (0.25 inch). Another couple was inserted in hole *M* in the orifice head.

Table II. Sources and Proximate Analyses of Coals Used

Sample No.	Seam	Location	Volatile Matter	Fixed Carbon	Ash
			%	%	%
1	Deepwater Black Creek	Nauvoo Mine, Nauvoo, Ala.	39.1	56.9	4.0
52	B or Lower Kittanning	Mine No. 37, Windber, Pa.	17.5	75.2	7.3
54	No. 2 Gas	Bridge Fork Mine, Anstead, W. Va.	36.1	61.0	2.9
55	Pittsburgh	Banning No. 1 Mine, Van Meter, Pa.	34.8	59.4	5.8
56	Lower Kittanning	Colver, Pa.	22.3	73.0	4.7
57	Imboden	Stonega, Va.	34.0	60.4	5.6

Table III. Screen Analyses of Coals Used

Coal No.	On 20 Mesh	On 28 Mesh	On 48 Mesh	On 80 Mesh	On 100 Mesh	Through 100 Mesh
	%	%	%	%	%	%
1	40.8	15.2	18.6	9.3	3.3	12.7
52	33.4	13.3	18.7	10.7	4.2	19.5
54	36.8	14.1	19.8	10.0	4.3	14.9
55	36.5	14.7	19.7	10.4	3.6	14.9
56	22.8	15.5	25.5	13.3	5.7	17.0
57	50.3	13.5	16.2	7.3	3.0	9.1

In running tests, the temperature of the apparatus was brought up to 300° C. at a rate of about 10° per minute and the rate of increase, as read in the orifice head, was then adjusted to 2° C. per minute. The temperature in the coal at 0.635 cm. (0.25 inch) above the orifice was taken just before extrusion pressure was applied, and the couple then removed. The temperature of the orifice head was observed during extrusion.

Preliminary measurements indicated that, at the beginning of the extrusion period, there was, on the average, a temperature difference of 8° between the steel orifice head and the coal 0.635 cm. (0.25 inch) above the orifice. Furthermore, there was a decreasing gradient of about 8° per cm. in the coal upward from the orifice. During extrusion this steady condition was disturbed somewhat, but the rise of temperature of the apparatus during extrusion tended to offset the temperature gradient in the coal column. The temperature of the coal passing through the orifice was therefore known only approximately, but was probably within a few degrees of that of the coal 0.635 cm. (0.25 inch) above the orifice at the beginning of the extrusion period.

The description, proximate analysis, and size composition of coals used in this investigation are given in Tables II and III.

Relation of Extrusivity to Temperature

Preliminary experiments revealed that extrusivity changes rapidly with temperature and that during an extrusion test the coal temperature must be confined to a relatively short interval. In Table IV are presented extrusion data on five coals.

In each series of tests the temperature of the coal at the start of extrusion was increased by intervals of 10° until the entire temperature range of plasticity of the coal had been covered. A standard pressure of 2.43 kg. per sq. cm. was applied to the piston except in the case of coal 52. The degree of plasticity developed by this low-volatile bituminous coal was so small that extrusion could only be secured by application of a pressure of 7.24 kg. per sq. cm. and by very rapid preliminary heating of the charge.

The temperatures listed in Table IV show the temperature range of plasticity for each coal; at temperatures lower than those listed the coal had not softened sufficiently to permit extrusion and at higher temperatures the formation of hard coke developed.

Table IV. Relation of Extrusivity and Temperature

Coal	Orifice Number	Initial Coal Temperature	Extrusivity
		° *C.*	*G./Min.*
54	5	410	0.55
		420	0.90
		430	1.59
		440	0.80[a]
55	5	410	0.85
		420	1.17
		430	0.75[a]
56	4	430	0.38
		440	0.59
		450	0.37[a]
57	4	410	0.62
		420	1.20
		430	1.05
52	3	500	1.15[a]

[a] Formation of hard coke prevented complete extrusion of the charge.

It is apparent that these coals attained sufficient plasticity to permit extrusion in a range of temperature that did not exceed 40°. Furthermore, the extrusivity varied rapidly with temperature and attained a maximum value for each coal.

Attempts were made to measure extrusivities at 1-minute intervals as the temperature of the tube was raised in a single test through the entire temperature range of plasticity. The impossibility of correctly recording the temperature of the coal as it passed through the orifice, however, prevented the successful completion of this project.

Correlation of Extrusivities and Other Data

Before comparing extrusivities, it was necessary to secure a factor that would place extrusivities determined by the No. 4 and No. 5 orifices on a comparable basis. The extrusivity of coal 57 was measured at the temperature of maximum plasticity, 420° C., with both the No. 4 and No. 5 sizes of orifice. From these tests it was found that extrusivities measured by the No. 4 orifice should be reduced by the factor 0.4 to make them comparable to extrusivities measured by the No. 5 orifice. No attempt was made to correct the one value with the No. 3 orifice because of its large diameter and the high pressure that was used with it.

In Table V the coals have been arranged in order of decreasing percentage of volatile matter. The volatile matter gives only a rough indication of the degree of extrusivity. Coal 1 with the highest percentage of volatile matter is almost nonfusing and coal 57 develops much less extrusivity than coal 54, although coal 57 has a higher volatile content. There is an approximate correlation between extrusivity and the temperature of initial softening and the temperatures maximum pressure as measured by the gas-flow test; extrusivity decreases as these temperatures rise.

Plastic Condition at Maximum Pressure

It will be noted in Table V that the temperatures of maximum pressure in the gas-flow test are in most cases less than the temperatures at which maximum extrusion occurs. This difference is important in view of the fact that the point of maximum pressure has been stated by some investigators to be the end of plasticity and the beginning of coke formation.

Table V. Correlation of Extrusivities and Other Data

Coal No.	Gas-Flow Test: Volatile matter	Gas-Flow Test: Initial fusion	Gas-Flow Test: Maximum pressure	Extrusion Tests: Initial temp. for max. extrusion	Extrusion Tests: Average extrusion
	%	° C.	° C.	° C.	G./min.
1	39.1	400	415–35	Not sufficiently plastic	
54	36.1	385	415	430	1.59
57	36.1	395	425	420	0.48
55	34.8	375	415	420	1.17
56	22.3	400	440	440	0.24
52	17.5	440	490	500	1.15[a]

[a] Uncorrected value obtained from the No. 3 orifice and by application of high pressure.

The difficulty of obtaining true coal temperatures in the extrusion test has been pointed out. To eliminate the possibility that the methods of measuring coal temperatures in the gas-flow and extrusion tests were not comparable, the extrusion apparatus was changed to permit carrying out both tests in the same apparatus in a single experiment.

A length of brass tubing was wrapped around the outside of the fusion tube, *O* (Figure 9) to serve as a preheating coil for nitrogen. The lower end of the preheating coil was fitted tightly into the orifice below the coal charge and the usual procedure for the gas flow test was then followed.

When the gas pressure had reached a maximum value and had begun to fall, the nitrogen tube was pulled away from the orifice, the piston inserted, and extrusion allowed to take place. By these combined gas-flow and extrusion tests, in which the possibility of error from the method of measuring coal temperature had been eliminated, the following data were secured and clearly show that coals are in a plastic condition at temperatures higher than that of the maximum gas pressure in the gas-flow test:

Coal	55	54
Temperature of maximum gas pressure, ° C.	415	427
Temperature of start of extrusion, ° C.	425	427
Time of extrusion, minutes	4.5	5.0
Amount of extrusion, grams	3.9	4.3
Extrusivity, grams per minute	0.87	0.86

Acknowledgments

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Estimation of Chloramine in Water Supplies

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THE widespread use of chloramine instead of chlorine for the disinfection of water supplies renders a distinctive test for chloramine desirable. At present, the chloramine content is measured by the *o*-tolidine test for residual chlorine. The limitations of this test are well known and interference by nitrite ions is especially notable. As pointed out by Hulbert (*3*), nitrite is usually formed in chloramine-treated water.

The hydrogen-ion concentration determines the type of chloramine present. According to Chapin (*2*), at pH 8.5 or above only monochloramine is formed and below pH 4.4 only nitrogen trichloride is produced. Between pH 4.4 and 8.5, mono- and dichloramine coexist in a ratio fixed by the pH of the solution. When sufficiently acidified, a solution of monochloramine is converted to nitrogen trichloride according to the equation

$$3NH_2Cl + 2H^+ \longrightarrow 2NH_4^+ + NCl_3$$

Marckwald and Wille (*4*) infer that the above reaction takes place in two steps:

$$2NH_2Cl + 4HCl \longrightarrow 2NH_4Cl + 2Cl_2 \quad (1)$$
$$NH_2Cl + 2Cl_2 \longrightarrow NCl_3 + 2HCl \quad (2)$$

and that the reaction is catalytically accelerated by liberated acid. In dilute solutions of chloramine, this reaction is very rapid, less than 1 minute being required to convert monochloramine to nitrogen trichloride at 15° C.

As indicated by the above equations, the chloramine content of a solution may be measured by determining the amount of ammonium ion formed on acidification. When the pH of a monochloramine solution is lowered to 4.4 or

below, two-thirds of the nitrogen present as chloramine is converted to ammonium ion. The chloramine-chlorine content is then obtained by multiplying the observed increase in ammonia-nitrogen by 3/2 × 35.5/14 or 3.8. When 50-ml. Nessler tubes are used, the factor becomes 3.8/5 or 0.76, which for convenience may be considered 3/4. (The Nessler tube readings correspond to milligrams of nitrogen per liter when 10-ml. samples are read.)

Procedure

Two 50-ml. Nessler tubes are filled with the solution to be examined. To one tube is added enough sulfuric acid (0.2 ml. of 1 to 10 solution) to lower the pH below 4.4, and the contents are mixed by inverting the tube, which is allowed to stand 1 minute. If the pH of the original solution was below 8.6, a small amount of sodium carbonate (0.1 ml. of 5 per cent solution) is added to the other tube and the contents are mixed. Two milliliters of Nessler reagent (*1*) are then added to each tube. The tubes are inverted to insure complete mixing and are compared with the standards after 1 minute. It is essential that the tubes be read not later than 1 minute after addition of Nessler reagent. A set of permanent standards (*1*) is prepared to match the colors developed in 1 minute by known amounts of ammonia and 2 ml. of Nessler reagent. Approximately 90 per cent of the full color is developed in 1 minute at 20° C.

Effect of Time

The effect of allowing the tubes to stand after the addition of Nessler reagent is shown in Table I.

Table I. Effect of Time

Time	Reading of Alkaline Tube	Reading of Acid Tube	Difference in Readings, Δ	Chlorine as Chloramine, 0.76 Δ
Min.				*P. p. m.*
0.5	0.6	1.6	1.0	0.76[a]
1.0	0.7	1.7	1.0	0.76
3.0	0.9	1.8	0.9	0.68
5.0	1.0	1.8	0.8	0.61
10.0	1.4	1.8	0.4	0.30

[a] The *o*-tolidine test gave a reading of 0.80 p. p. m.

Marckwald and Wille (*4*) assume the existence of an equilibrium,

$$NH_2Cl + H_2O \rightleftharpoons NH_3 + HClO$$

Removal of the ammonia by any reagent would impel the reaction toward the right. Fortunately, this reaction proceeds at a much slower rate than the production of color by Nessler reagent. Since the test depends on the difference in the readings of two tubes, both of which are becoming darker, the error introduced by a delay of one minute is very small. Serious errors are introduced, however, if the tubes are not read for several minutes.

Comparison with *o*-Tolidine Test

With relatively pure solutions of chloramine, the agreement between the proposed procedure and the *o*-tolidine method is excellent, as is shown in Table II.

Table II. Comparison of Procedures

Test Employed	Chlorine as Chloramine, P. p. m.							
o-Tolidine	0.32	0.35	0.30	0.27	0.38	0.37	0.30	0.30
Proposed	0.30	0.38	0.30	0.22	0.38	0.38	0.30	0.30

In this experiment, Cincinnati tap water was used, the nitrite-nitrogen content of which varied between 0.001 and 0.003 p. p. m. With a solution containing 0.2 p. p. m. of chloramine-chlorine and 0.5 p. p. m. of nitrite-nitrogen, the proposed method showed 0.22 p. p. m. of chloramine chlorine, while the *o*-tolidine method gave an apparent chlorine content of 0.45 p. p. m. Solutions containing varying amounts of nitrite but no chloramine all gave negative results with the proposed test, while the readings obtained with the *o*-tolidine test varied with the nitrite concentration. With solutions containing both chloramine and free chlorine, the test indicates only the chloramine.

Estimation of Free Chlorine

When free chlorine is present its amount may be determined by adding enough ammonia to the sample to convert all the chlorine to chloramine and then again determining the chloramine present. The difference in the two determinations is a measure of the original free chlorine.

Results obtained on solutions prepared from known amounts of ammonium ion and chlorine are shown in Table III.

Table III. Presence of Free Chlorine

Ammonia-Nitrogen Added	Chlorine Added	Reading of Tubes		Chlorine as Chloramine	
		Acid	Alkaline	Found	Theory
P. p. m.	*P. p. m.*			*P. p. m.*	*P. p. m.*
0.05	0.50	0.2	0.0	0.15	0.13
0.10	0.50	0.4	0.0	0.30	0.25
0.15	0.50	0.5	0.0	0.38	0.38
0.20	0.50	0.8	0.2	0.45	0.50
0.30	0.50	1.4	0.8	0.45	0.50

In this experiment varying amounts of a stock solution of ammonium chloride were added to ammonia-free water which contained 1 ml. of 5 per cent sodium carbonate. The chlorine solution was then added and the volume was brought to 1 liter with ammonia-free water. The chlorine content of the stock solution was determined iodometrically.

To that preparation which had been found to contain 0.15 p. p. m. of chlorine as chloramine there was added an additional 0.12 p. p. m. of nitrogen as ammonium chloride. The chloramine chlorine content was then found to be 0.45 p. p. m. On subtracting 0.15 from 0.45, the value of 0.30 p. p. m. was obtained for free chlorine in the original material. Actually there was added 0.50 p. p. m. of total free chlorine, so that there should have been 0.50–0.13 or 0.37 p. p. m. of free chlorine.

Sensitivity

This test for chloramine is not as sensitive as the *o*-tolidine test for free chlorine. Good results are obtained when the solution contains 0.2 mg. of chloramine chlorine per liter. The presence of relatively large amounts of free ammonia in the sample naturally reduces the precision of the test and for this reason it is of little value when applied to sewage or sewage-plant effluents.

Summary

Chloramine may be estimated through a determination of ammonium ion formed therefrom on acidification. The described method is especially useful in presence of nitrite and for differentiation between chloramine and free chlorine.

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Control of Forms of Iron in the Determination of Fusion Temperatures of Coal Ash

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THE degree of oxidation of the iron in coal-ash slags affects the temperatures at which the various stages of fusion occur; therefore control of oxidation is necessary in investigating the properties of such slags. This necessity occurred in studies (*4*, *5*) of slags and ashes associated with slag-tap furnaces. Of main interest was the temperature at which slag would flow with a definite degree of freedom, arbitrarily fixed as a viscosity of 10 poises compared with castor oil; this temperature was defined as the "flow temperature" and was determined by melting the sample of slag in a cylindrical crucible 0.75 inch in diameter and estimating the fluidity by means of a platinum rod. All determinations were made on the heating cycle, the stirring of the slag requiring progressively less effort until finally practically no resistance is felt to vertical movement of the rod, horizontal movement is but slightly impeded, and the slag flows immediately into the trough left by the passing rod. The lowest temperature at which these three conditions occur is the flow temperature; at higher temperatures it is not feasible to estimate fluidity by this method because of the poor retention of the rod in the slag. The flow temperature represents a transition point between a highly viscous slag where stirring will deform the rod, and a highly fluid slag where a large change in temperature makes no apparent change in the "feel." The training of investigators to recognize the desired fluidity has not been difficult. The effect of the state of the iron on the flow temperature has been reported (*5*).

The studies required control of the forms of iron to obtain slags having forms of iron in equilibrium with air at the flow temperature, to prevent change in the forms of iron during the determination of the flow temperature of slags taken from furnaces, and to produce in the laboratory slags having predicted forms of iron at the flow temperature.

This paper describes the apparatus and methods used to control the forms of iron and gives some of the results. It shows that the control specified in the preceding paragraph can be obtained but that further investigations of coal ash systems are necessary before the work can be done without subsequent analysis for forms of iron. The studies of the methods described were not carried to a higher order of accuracy than the operating conditions to which they were to be applied—namely, slagging and clinkering in furnaces.

Furnaces Used

The method of determining the flow temperature made it necessary to design the furnaces so that the operator could insert a platinum rod into the slag to feel its fluidity. Three furnaces were used. The first (*4*) was built for the earliest work, which was confined to determinations in air, the forms of iron assuming values in equilibrium with air.

The second furnace was gas-fired and was a modification of a design by Norton (*6*); the mixture of gas and air, or oxygen could be preheated by a preheater built into the base. Temperatures were read with an optical pyrometer with a right-angle prism to facilitate observation on the surface of the slag.

Figure 1 shows the design of the third furnace. This is electrically heated and the atmosphere in it can be controlled.

Eighty per cent platinum and 20 per cent rhodium wire was more satisfactory for the high-temperature winding than was a wire with 10 per cent rhodium. Its life is approximately 3000 hours with an effective furnace temperature not higher than 1500° C.; after 3000 hours the center section is reduced by volatilization, so that frequent repairs are necessary. The rate of heating above 1100° C. is limited to 10° C. per minute to prevent overheating of the wire. The auxiliary winding of nichrome is operated at approximately 1000° C. and has never failed. The crucibles are 96 per cent platinum and 4 per cent rhodium, 0.75 inch in diameter and 1.5 inches high, with 3 lugs equally spaced at top and bottom to centralize them in the furnace. Porcelain crucibles of the same diameter, but 2 inches high, are used for exceptional reduction of forms of iron by carbon.

The gas used for the atmosphere is admitted in three portions. One, admitted at *A* and *B*, sweeps out the main body of the furnace; another enters through the porcelain tube supporting the crucible, the tube being closed at the top and having 3 slots cut in it; the third portion impinges directly on the surface of the slag.

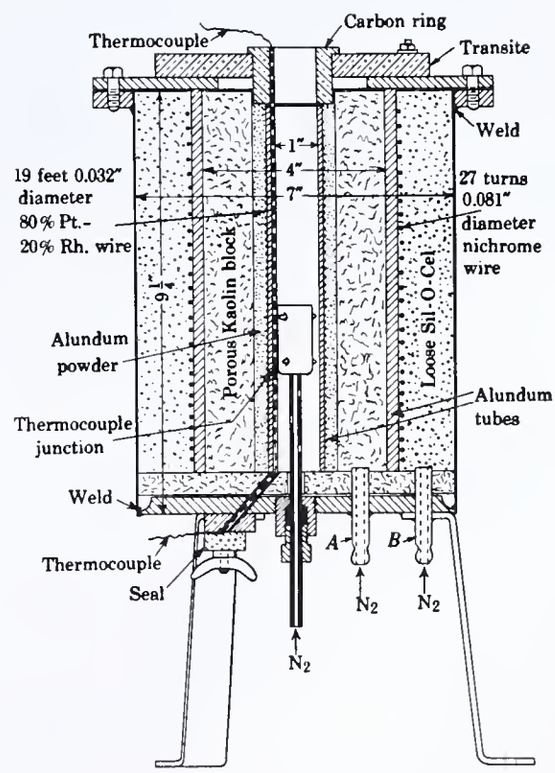

FIGURE 1. ELECTRIC FURNACE FOR MELTING COAL ASH IN AN ATMOSPHERE OF NITROGEN

Nitrogen is used to produce the inert atmosphere; Figure 2 shows diagrammatically the purification system finally adopted.

The nitrogen first passes through calcium chloride, then slowly over copper gauze heated to 400° C. in a small electric furnace, and then again through calcium chloride. The copper gauze is reduced each morning by heating it to a bright red in a reducing gas flame and then plunging it into alcohol. The purified nitrogen is distributed so that 1.0 cubic foot per hour passes into the bottom of the furnace and 0.5 cubic foot over the surface of the slag; assuming 50 per cent free space in the furnace and a mean temperature of 1100° C., there will be 50 changes per hour.

Preliminary Tests of Nitrogen Furnace

The primary purpose of the nitrogen furnace was to obtain the fusion temperature of coal-ash slags without changing the state of reduction of the iron. The initial tests were to determine the conditions necessary for such results. The term "ferric percentage" was adopted to express the degree of oxidation of the iron and is defined as the actual ferric iron content as a percentage of the total equivalent ferric iron; it is expressed by:

$$\text{Ferric percentage} = \frac{Fe_2O_3}{Fe_2O_3 + 1.11\ FeO + 1.43\ Fe} \times 100$$

in which the chemical symbols represent the percentages given by chemical analysis of the slag or ash. Coal-ash slags and ashes taken from furnaces have had ferric percentages ranging from 2 to 84.

Other investigators (*1*) have reported difficulty in obtaining nitrogen sufficiently free of oxygen to be inert to ferrous and metallic iron. These first tests were attempts to prevent such oxidation; a slag having a medium ferric percentage of 30.4 was used. In each test the slag was melted, the flow temperature determined, and the sample removed and immediately quenched in water; the forms of iron were then determined by analysis.

Figure 3 shows the variation in the ferric percentage with different melting conditions. Points 1 to 6, inclusive, show the effect on the ferric percentage of the presence of residual oxygen in the nitrogen over the surface of the slag. They also show that low concentrations of oxygen were nearly as effective in oxidizing molten slag as was air. Point 7, where at most a trace of oxygen was present, still indicates partial oxidation. Points 8 and 9, where all the nitrogen entering the furnace has had residual oxygen burned to carbon monoxide by contact with hot carbon, represent the conditions under which slag can be melted without oxidation.

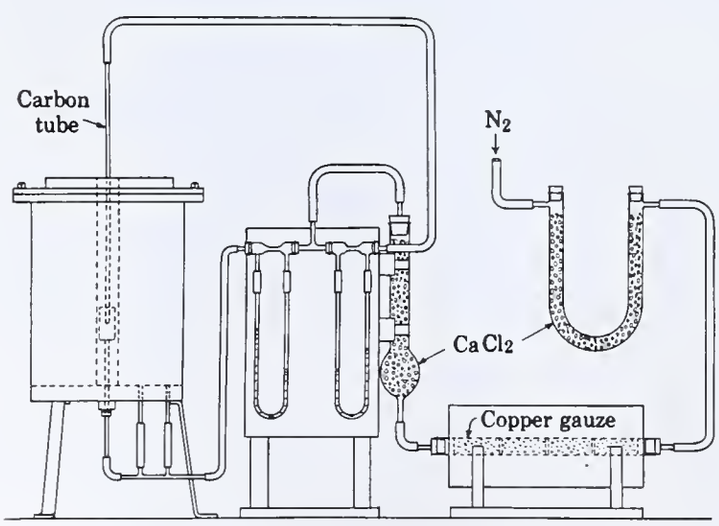

Figure 2. Nitrogen Purification System

The presence of oxygen, after the nitrogen has passed over copper at 400° C., is indicated by the formation of a pear-shaped hollow in the bore of the carbon tube about 3 inches above its lower end. Above 1000° C. there is less than 1 per cent of carbon dioxide in the equilibrium of carbon dioxide, carbon monoxide, and carbon (*3*), so that the impurities in the nitrogen should be limited to a trace of carbon monoxide.

Although oxidizing gases probably are not present in the furnace, there is the possibility of reduction; therefore it has become routine to determine the forms of iron after each test. Further modifications of the methods for purification of the nitrogen have not been tried; the elimination of direct contamination by carbon would be the next development.

Two further precautions are observed to prevent initial oxidation. The furnace is heated for one hour before introducing the slag, so that the nitrogen can displace air drawn into the furnace since the previous run. The slag is held at 700° C. for 20 minutes with occasional stirring to release any air in the 60-mesh charge before it is heated to the point where oxidation would be rapid.

Tests of Slags

The slags were samples from slag-tap furnaces; they were ground to pass 60-mesh, melted in the nitrogen furnace, and analyzed for forms of iron. Such slags generally contain less than 0.01 per cent of carbon, but during periods of poor operation combustible from the surface of the bed may be mixed with the slag as it flows from the furnace; this carbon will further reduce the iron oxides when the slag is remelted.

Table I shows the results obtained in the nitrogen furnace; the items are arranged in order of increasing total equivalent ferric oxide in the slag. The last column shows the change in ferric percentage from that of the original slag; a small change in the oxygen content makes a greater change in the ferric percentage for low than for high total equivalent iron.

Table I. Melting of Slags in the Nitrogen Furnace

		Analysis, Per Cent						Ferric Percentage		
		Before			After					
Item	Slag No.	Fe_2O_3	FeO	Fe	Fe_2O_3	FeO	Fe	Before	After	Difference
1	362	0.3	8.0	0.1	0.1	8.0	0.2	3.2	1.1	− 2.1
2	404	0.7	6.5	1.5	1.1	5.4	2.0	7.0	11	+ 4
3	321	1.4	8.5	0.3	1.0	8.8	0.3	12	8.9	− 3.1
4	381	1.4	8.5	0.8	2.6	7.6	0.6	12	22	+10
5	338	3.1	7.7	0.4	2.8	8.2	0.3	25	23	− 2
6	356	3.9	7.2	0.4	2.6	8.3	0.5	31	21	−10
7	334	4.4	7.3	0.3	1.9	9.4	0.4	34	15	−19
8	Dup.	4.4	7.3	0.3	2.2	9.1	0.4	34	17	−17
9	348	0.3	12.3	0.4	1.5	11.5	0.2	2.1	10	+ 7.9
10	Dup.	0.3	12.3	0.4	1.5	11.4	0.3	2.1	10	+ 7.9
11	344	0.1	11.3	0.3	0.9	10.6	0.3	0.8	6.9	+ 6.1
12	410	5.3	13.1	0.2	3.1	15.0	0.3	26	15	−11
13	388	2.2	15.6	1.3	2.0	14.4	2.4	10	9.3	− 0.7
14	407	4.1	15.7	0.6	2.4	17.2	0.6	18	11	− 7
15	423	5.9	21.7	0.9	5.1	22.3	1.0	19	16	− 3
16	359	4.0	23.8	1.1	2.7	24.0	1.9	12	8.4	− 3.6
17	421	7.6	21.0	1.1	7.2	21.6	0.9	23	22	− 1
18	325	2.7	25.9	2.7	3.5	25.0	2.8	7.6	10	+ 2.4
19	227	11.3	21.8	1.2	10.5	21.7	1.9	30	28	− 2
20	205	9.0	22.6	5.5	10.6	25.8	1.5	21	26	+ 5

Five slags were oxidized, but no assured explanation can be offered as to the source of the oxygen. Adsorption of air by some slag surfaces may be greater than by others and thus the removal of the air by displacement with nitrogen will be less complete; in this way oxidation may have occurred during the initial heating. Moreover, it might occur during the removal of the slag from the crucible prior to quenching. Item 10 is a check melt on item 9; the agreement of the results shows that the cause of oxidation was the same in both melts.

The greatest reduction during melting was that of the slag of item 7; item 8 was a duplicate melt. Analysis of the original slag showed 0.25 per cent of carbon.

Production of Definite Ferric Percentages

The determination of the relation between flow temperature and degree of reduction necessitated variation of the latter between high and low values. Four methods of producing these variations in the ferric percentage were used: reducing an oxidized slag in the gas furnace; mixing different proportions of the same slag, one part having a low and the other a high ferric percentage; partly oxidizing a reduced slag by heating it in air and transferring it to the nitrogen furnace; and adding carbon to either oxidized ash or partly reduced slag.

No data are available on the atmosphere in the gas furnace necessary to produce a desired reduction. Matsubara (*2*) has shown the relationship of iron, carbon, and oxygen, but these relationships do not apply in the presence of silicates; moreover some hydrogen and methane are present in the gas furnace. Most of the reduction takes place before the ground slag melts because a large surface is exposed, but after melting the rate of reduction is low because the gas diffuses slowly through the molten slag; thus there is a lag between change of atmosphere and change in forms of iron once the slag has been melted. Even if data were available, the exact composition of the gases in contact with the slag would not be known because combustion may not be complete in the small space above the crucible. The use of a larger combustion space results in a greater loss of heat and consequently in a lower temperature. In a highly reducing atmosphere an unknown quantity of carbon may be deposited on the slag and the reduction greatly increased.

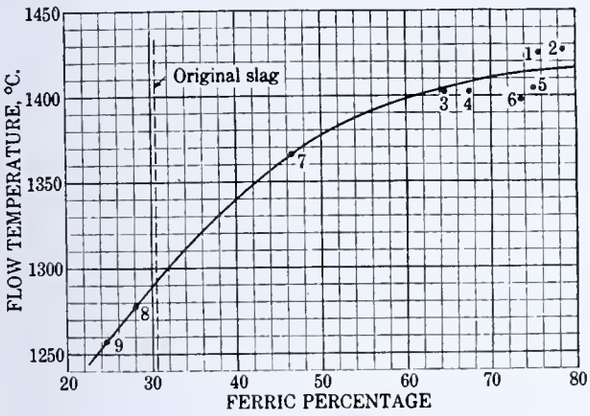

FIGURE 3. VARIATION IN FERRIC PERCENTAGE OF A SLAG UNDER DIFFERENT MELTING CONDITIONS

1. Melted in air to obtain reference value.
2. Melted in unpurified nitrogen, using porcelain tube above crucible.
3, 4. Melted in unpurified nitrogen, but rate of supply increased three times; none supplied over crucible.
5. Same as 2, but nitrogen passed through sulfuric acid, calcium chloride, and sodium pyrogallate and finally dried over calcium chloride.
6. Same as 5, except that no nitrogen was admitted at surface of slag. At this stage leakage of air into the furnace was suspected, and the carbon ring shown in Figure 1 was added to seal the inner cylinder.
7. Melted in nitrogen purified by passage over hot copper gauze; bottom of the inner cylinder packed with carbon. Porcelain tube, as in 2, was used to admit nitrogen over surface of slag.
8. Same as 7, but carbon tube was used in place of porcelain to supply nitrogen over surface of slag.
9. Same as 8, but fragment of carbon tube fell into slag; although carbon was immediately removed, partial reduction of slag had taken place.

There were a number of objections to the gas furnace method. The porcelain of the crucibles could contaminate the slag or preferentially absorb iron oxides; temperature measurements by sighting on the surface of the slag were not satisfactory; the rate of change of temperature was difficult to control; and there was the possibility that the degree of reduction was not uniform throughout the slag.

The second method, that of mixing, required the preparation of two portions of ground slag, one having a low and the other a high ferric percentage but otherwise of the same composition. The reduced slag was ground to pass 60-mesh and riffled into two portions, one of which was oxidized in a muffle furnace at about 700° C.; as an alternative method a smaller portion was oxidized by melting in a platinum crucible in air.

Table II summarizes the results of the melting tests; the slag was T-348, item 9 of Table I. Previous work showed that when a slag is melted in air it attains the same ferric percentage whether the original ferric percentage is high or low; thus A and B gave 57 and 59, respectively. However, when melted in nitrogen, B, with an original ferric percentage of 70, was reduced to 18 (19 in a repeat test) and C, originally 57, was reduced only to 48. The natural deduction is that oxidation by the two methods yields slags in which the iron oxides exist in different combinations or solutions. Possibly the ferric oxide in the slag oxidized in the muffle is less firmly held; the typical brownish red color of the oxidized material supports this supposition. A mixture of A and C would be expected to give a higher ferric percentage than a mixture of A and B, but items F and G show that the results were approximately the same.

TABLE II. FERRIC PERCENTAGE BY MIXTURES

Item	Slag or Mixture	Ferric Percentage: Before melting	After melting: In air	After melting: In nitrogen
A	Original	2	57	10
B	From muffle	70	59	18 and 19
C	From air-furnace	57	..	48
D	90 per cent A	2	..	26
	10 per cent B	70	..	..
E	70 per cent A	2	..	22
	30 per cent B	70	..	..
F	50 per cent A	2	..	16
	50 per cent B	70	..	..
G	50 per cent A	2	..	15
	50 per cent C	57	..	..

In the third method a reduced slag was ground to pass 60-mesh, partially oxidized in the air furnace, and then transferred quickly to the nitrogen furnace to prevent further oxidation. This method was used in a few instances when the exact values for the ferric percentage were not important. More data are required on the relation of rate of oxidation to temperature and time before this method can be used to obtain definite ferric percentages.

An example of the fourth method (reduction by adding carbon to an oxidized slag) was when the iron content of a slag was increased by adding ferric oxide. The ground slag, ferric oxide, and lampblack were mixed intimately by grinding them in an agate mortar, and the mixture was melted in a platinum crucible in the nitrogen furnace. The results obtained are illustrated by tests in which slag 356 (item 6, Table I) was used. This slag contained 12.5 per cent of equivalent ferric oxide and had a ferric percentage in the nitrogen furnace of 21. Two other slags were made from it by adding ferric oxide as 5 and 10 per cent, respectively, by weight of the original slag. Table III shows the results.

TABLE III. REDUCTION BY ADDING CARBON

Item	Additions: Fe_2O_3	Additions: Carbon	Ferric Percentage: Computed	Ferric Percentage: By test	Maximum Temperature
	%				° C.
1	5	...	44	29	1366
2	5	Yes	15	16	1343
3	10	...	56	50	1343
4	10	Yes	11.6	12	1266

The test values of the ferric percentage of items 1 and 3, melted without the addition of carbon, are lower than the computed values because of thermal decomposition of the added ferric oxide. Decomposition in nitrogen begins at 1150° C., and the conversion to magnetite is complete at 1400° C. (*7*), but these values may not be correct when the ferric oxide is mixed with slag. In item 1, the slag was heated to a higher temperature than in item 3 and more dissociation would occur. The quantity of carbon added for items 2 and 4 was on the basis of $Fe_2O_3 + C \rightarrow 2FeO + CO$. This reaction starts at 600° C. and would be completed before thermal decomposition could occur; therefore the computed is close to the test value.

The choice of methods to be used to produce definite ferric percentages will depend upon the facilities and the objectives. In this investigation highly reduced slags having a wide range of composition were available; therefore oxidation by heat-

ing individual samples in air, or by oxidizing a larger sample and using the method of mixtures, was most satisfactory. When the investigation uses synthetic mixtures or ignited coal ashes, reduction by addition of computed amounts of carbon would be the most direct method. All the methods lack assured precision and chemical analyses of the melts are necessary; determination of ferrous oxide is generally all that is required except for the most exact work.

Acknowledgments

These investigations were conducted at the Pittsburgh Experiment Station of the U. S. Bureau of Mines under the immediate direction of P. Nicholls. The chemical analyses were made by W. H. Frederic under the direction of W. A. Selvig.

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Determining the Specific Gravity of Gases

Improvements in the Effusion Method

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THE effusion method for determining the specific gravity of gases (*2*, *3*) has been widely employed, because of the simplicity of the apparatus and its manipulation, although it has been generally recognized that the results obtained can in most cases be regarded only as approximations in view of what were considered to be inherent errors in the method. It is toward the minimization of such errors that the work discussed in this paper was directed.

In so far as could be determined, little work had been done in improving the accuracy of the effusion method since its inception in the seventeenth century until about 1917, when Edwards published (*1*) the results of an extensive investigation of the effusion method of determining gas density. In spite of the soundness of the conclusions and recommendations presented, they apparently received little consideration and certainly had not been put into practice at the time the work herein under discussion was undertoken.

Apparatus and Operation

Following unsuccessful attempts typified by Figure 1 to develop a satisfactory correlation between the results obtained with a standard make of effusion bottle and with an Edwards specific gravity balance (previously calibrated by means of pure gases), a careful study of the operating technic was made.

This, however, failed to reveal any source of appreciable error and attention was accordingly directed to the equipment. Bearing in mind that Edwards had stressed the necessity of having a carefully prepared orifice, the plate was removed from the apparatus and subjected to microscopic examination. Even a casual inspection (upper left, Figure 2) is sufficient to establish its inferiority. Closer inspection indicates that the irregularities are due to the employment of a punch in effecting the opening, and indeed such a procedure is generally recommended in the literature.

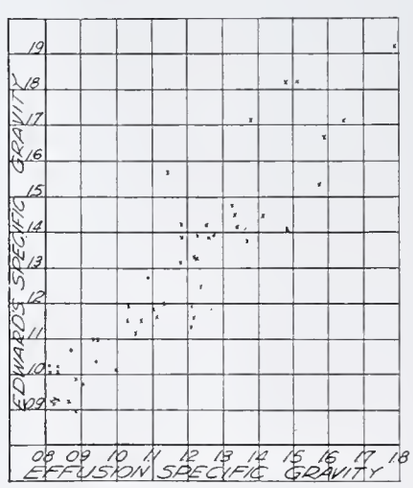

Figure 1. Correlation of Results with Standard Effusion Bottle and Edwards Specific Gravity Balance

Preparation of Orifice. After some experimentation a method was developed whereby a round and burr-free orifice opening could be effected.

A regular steel needle is carefully turned down by means of fine emery so that a very fine, long, and tapering point is obtained. Using this needle, the orifice plate is punched very lightly as nearly in the exact center as possible and the protruding metal is carefully removed by a twist drill (size 80, approximately) run along the side of the plate. The needle drill is again used and, working from both sides of the plate, the opening is increased to the desired size. This operation requires much care and patience and frequent examination under the microscope should be resorted to in order to insure proper roundness of the opening and freedom from burrs and to avoid increasing the diameter above the desired amount. An orifice prepared in this way is shown in the upper right-hand photomicrograph, Figure 2.

With an orifice prepared in the manner described, a correlation such as that shown by Figure 3 was obtained by determining the specific gravities of a wide range of refinery gases on both the effusion bottle and the Edwards balance. The average deviation of these results from the correlating line is negligible and, except for one sample showing a negative deviation of 6 per cent, the maximum deviations are less than 5 per cent. In this instance the effusion bottle results are approximately 5 per cent lower than those obtained with the Edwards balance.

Enlargement of Gas Chamber. In order to effect further improvement in the accuracy of the method, consideration was given to means of obtaining an increased time of flow. It was finally decided to accomplish this through increasing the size of the calibrated chamber in preference to reducing the size of the orifice, since the latter procedure is objectionable both from a standpoint of increased tendency to error through plugging of the orifice and of difficulty in preparing a smaller

orifice which is satisfactorily round and burr free. Figure 4 shows the revised apparatus in some detail; the chamber volume has been increased from 100 to 200 cc.

Figure 5 presents the results obtained with the revised equipment correlated with results obtained with an Edwards balance on gases of approximately the same range of specific gravity as previously employed. In this instance the average deviation from the correlating line is less than 0.1 per cent, with maximum positive and negative deviations of 4.5 and 2.9 per cent, respectively. The effusion results are, on the average, 2.75 per cent lower than those obtained with the Edwards balance.

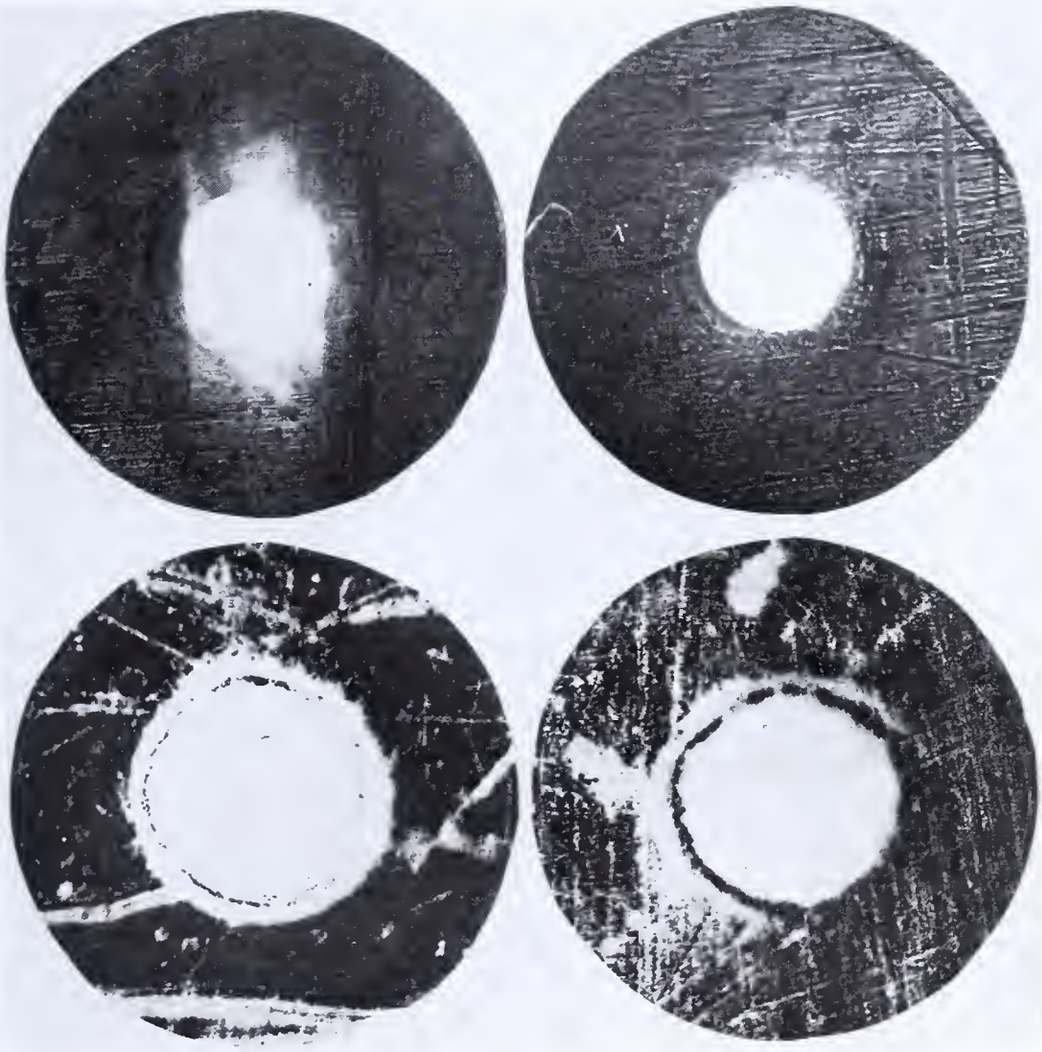

Figure 2. Photomicrographs

Stainless Steel Orifice. Figure 6 presents the results obtained with an effusion apparatus employing the enlarged chamber and an orifice (lower left, Figure 2) having an opening 0.240 mm. in diameter in a sheet of stainless steel 0.052 mm. thick. These results, in which the average deviation is less than 0.3 per cent and the maximum positive and negative deviations are 2.61 and 1.64 per cent, respectively, simply indicate that stainless steel may be substituted for platinum where service conditions will permit. It is entirely probable that other metals which can be obtained in satisfactorily thin sheets can be employed as particular conditions encountered may warrant.

Effect of Orifice Diameter and Plate Thickness on Accuracy. Figures 7 and 8 present the results obtained with two platinum orifices, one (lower right, Figure 2) having an opening 0.300 mm. in diameter in a plate 0.092 mm. thick and the other having an opening 0.260 mm. in diameter in a plate 0.130 mm. thick. The results of these determinations, as well as the two previously discussed, are summarized in Table I.

While it is realized that above data are inadequate to establish definite limits as to the size of the orifice opening or the thickness of the plate, it is believed justifiable to set up an

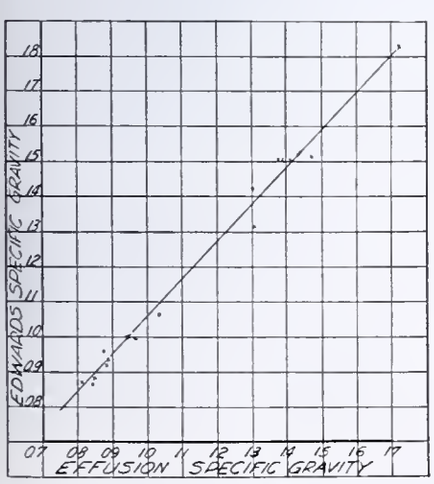

Figure 3. Correlation of Specific Gravity Determinations

Using orifice prepared by author's method

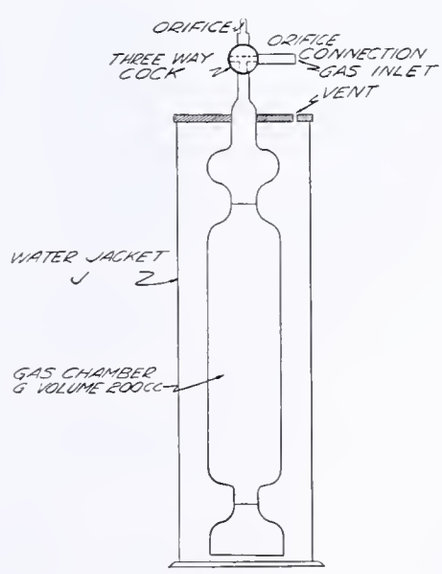

Figure 4. Revised Apparatus

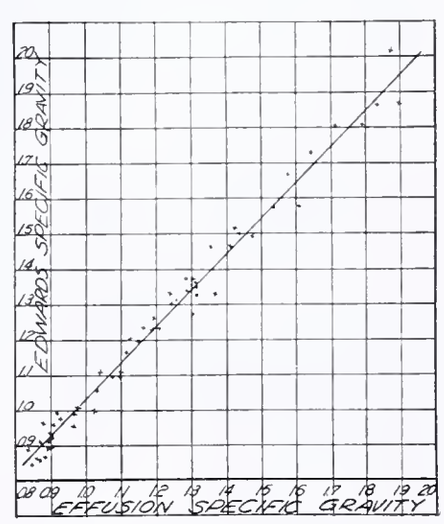

Figure 5. Correlation of Results with Revised Equipment and Edwards Balance

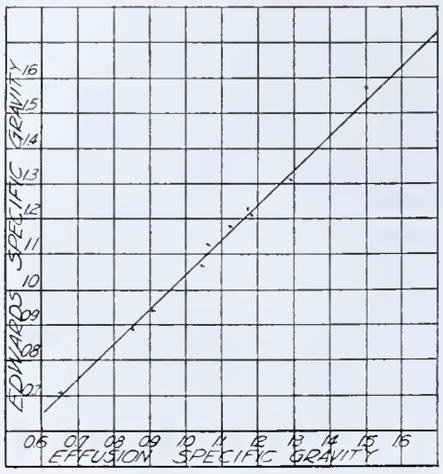

FIGURE 6. RESULTS WITH ENLARGED CHAMBER AND STAINLESS STEEL ORIFICE

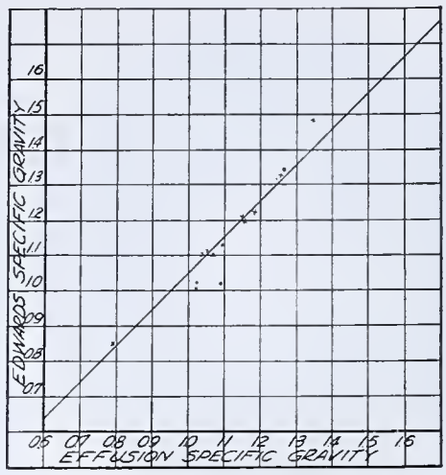

FIGURE 7. RESULTS WITH PLATINUM ORIFICE

Lower right, Figure 2

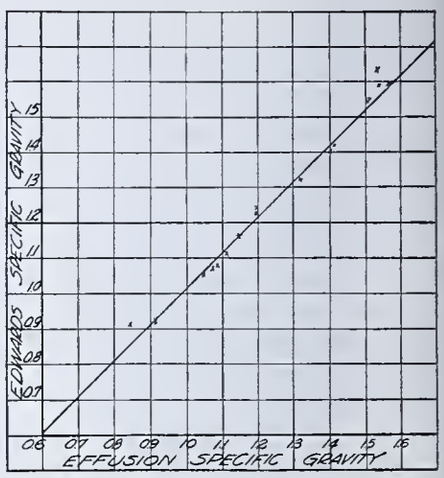

FIGURE 8. RESULTS WITH PLATINUM ORIFICE

opening of approximately 0.240 mm. diameter in a plate of less than 0.10 mm. thickness as a tentative standard. Experience has indicated that difficulty is encountered in obtaining round, smooth openings of a diameter less than 0.200 mm. and this should be the lower limit. The results indicate that, at 0.300 mm. diameter, the operation is unsatisfactory so that the diameter should propably not exceed 0.260 mm. It is believed desirable to employ as thin a sheet as possible with due regard to providing sufficient strength to resist normal wear. Anything above 0.05 mm. should be satisfactory in this respect. Considerably more importance should be attached to the diameter of the opening than to the thickness of the plate.

TABLE I. RESULTS OBTAINED WITH VARYING ORIFICE DIAMETERS AND PLATE THICKNESSES

Orifice Plate Thickness	Orifice Diameter	Percentage Deviation From Edwards	Percentage Deviation Maximum from curve Positive	Percentage Deviation Maximum from curve Negative	Reference Figure No.
Mm.	*Mm.*				
0.052	0.240	−3.64	2.61	1.64	6
0.130	0.260	−2.15	7.02	6.00	8
0.110	0.188	−2.75	4.54	2.92	5
0.092	0.300	−4.85	5.72	6.46	7

ELIMINATION OF CONDENSATION ON ORIFICE. In order to eliminate, if possible, the tendency towards accumulation of small drops of water around the orifice, attempts were made to employ acidified solutions of zinc sulfate and ferrous sulfate as confining media in the effusion bottle. Considerable difficulty was encountered, however, with precipitation of zinc sulfide and iron sulfide in the bottles and no improvement in the accuracy was obtained. Predrying of the samples just before entering the apparatus likewise had no apparent effect on the accuracy of the method.

DECREASED ACCURACY AT HIGHER SPECIFIC GRAVITIES. An inspection of the graphical presentations shows that the greatest deviations occurred for the most part in the specific gravity range above 1.30. This may be attributed to the tendency towards condensation of some of the heavier components of the gas around the orifice. It was attempted to eliminate this effect by placing the entire apparatus in a thermostatically controlled box so that determinations might be made at a higher temperature. This, however, was not found satisfactory, because of increased vaporization of the water used as the confining medium. Since, at the present time, there appears to be no way of improving the accuracy in the higher gravity range, it is recommended that the results so obtained be accepted only with reservation.

Sources of Error

Experience with the effusion method has indicated that the following avoidable factors may contribute to inaccurate results: (1) loss of confining medium between determinations, (2) leakage of the apparatus, (3) accumulation of dirt in the orifice.

The air rate should be frequently checked to insure that no radical change has occurred which might indicate the influence of one of the above factors. It has also been found advisable to clean the orifice periodically by washing with alcohol and ether. A clean hair may be used to remove any accumulated material from the opening. If possible the orifice should be examined occasionally under a microscope to insure its being in a satisfactory condition.

CALIBRATION OF EACH ORIFICE. Included in Table I is a column showing the per cent deviation from Edwards which varies from 2.15 to 4.85 per cent, the effusion results being too low in every case. It is for this reason recommended that, wherever possible, each orifice be calibrated against an Edwards balance or by means of gases of known specific gravity. In the event no method of calibration is available it is recommended that the specific gravity as determined directly from the effusion apparatus reading be arbitrarily increased by 2.5 per cent.

Conclusions

The results obtained in this work are such as to warrant the acceptance for routine work of gas specific gravities below 1.30 obtained by the effusion method employing the enlarged gas chamber and corrected by means of a correlation of the apparatus being used with a specific gravity balance. The probable accuracy so obtained is within 2.5 per cent. Values above 1.30 may be used, but the probable accuracy is considerably lessened above that figure.

The data, although not entirely conclusive, indicate that the orifice plate should have a thickness of less than 0.10 mm. and probably above 0.05 mm. The diameter should be approximately 0.240 mm. and should not exceed 0.260. Below 0.20 mm. diameter difficulty is encountered in obtaining a satisfactory opening.

Stainless steel is recommended as an acceptable substitute for platinum in making the orifice plate for service where stainless steel will withstand the corrosive agents present.

Acknowledgment

Considerable thanks are due to G. C. Fairbairn of The Texas Company for his assistance in developing a suitable drill

for the production of satisfactory orifice openings and in other phases of the work.

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A Line-Operated Vacuum-Tube Voltmeter

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SINCE the introduction by Goode (*4*) of the vacuum-tube device for measurements in electrochemistry, many circuits employing this device have been described (*3*). In general they have been battery-operated and in many cases of single-tube assemblies their sensitivity has proved inadequate.

The recent circuits of Dubridge (*1*, *2*) and others (*7*, *9*) have been designed for high sensitivities. The same principles may be used in the construction of a line-operated device. However, it is impossible to attain the same degree of stability without an accompanying loss of sensitivity because of the high line-voltage fluctuations as compared to battery fluctuations.

The balanced single-tube circuits of Dubridge and Turner were designed primarily for special electrometer tubes in which the filament formed part of the balancing network. The direct adaptation of these circuits to ordinary commercial radio tubes, where alternating current line operation is desired, proves difficult in practice because of the necessity of rectifying the relatively high filament currents (0.3 to 2.5 amperes).

The bridge circuits of Wynn-Williams (*10*), Nottingham (*6*), and others (*5*) avoid this difficulty, but depend upon the selection of matched tubes for successful operation.

A stable and yet sensitive circuit which will operate from both alternating and direct current lines can be designed by combining the mu-balance (*8*) and conventional bridge circuits. A circuit design based on these considerations which was found practical is shown in Figure 1.

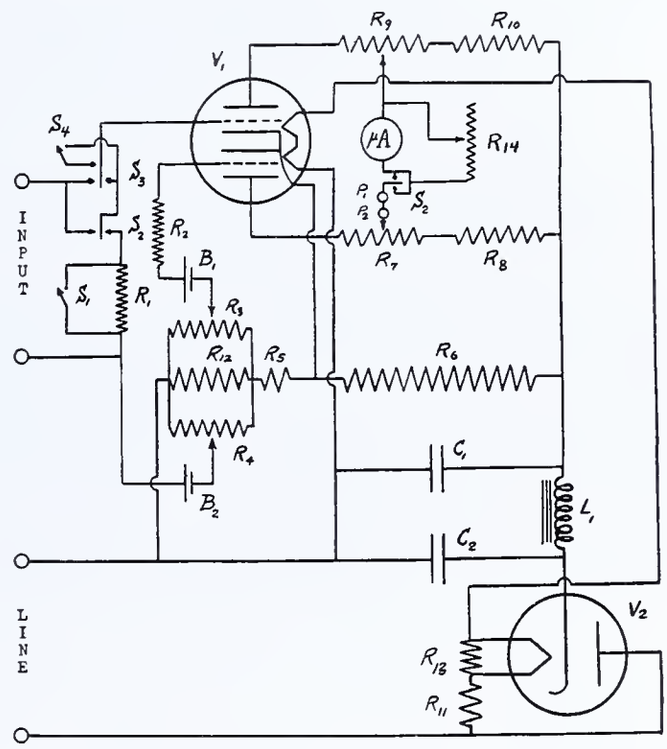

FIGURE 1. CIRCUIT DESIGN

R_1, R_2.	1 megohm, 1 watt	C_1, C_2.	8-mfd. electrolytic condenser
R_3, R_4.	400-ohm control	S_1.	S. P. S. T. Yaxley jack switch
R_5.	200 ohms, 15 watts	S_2.	D. P. D. T. Yaxley push-button switch
R_6.	8000 ohms, 30 watts	S_3.	D. P. D. T. Yaxley jack switch
R_7, R_9.	5000-ohm control	S_4.	S. P. S. T. Yaxley jack switch
R_8, R_{10}.	20,000 ohms, 2 watts	V_1.	6A6
R_{11}.	140 ohms, 100 watts	V_2.	84
R_{12}.	300 ohms, 15 watts	μA.	Weston 0-200 microammeter
R_{13}.	20 ohms, 15 watts		
R_{14}.	10,000-ohm tapered control		
L_1.	30 H. choke, 200 ohns		
B_1, B_2.	3v. flashlight batteries		

A duo-triode (6A6) tube is used in which the plate impedances of the tube form two arms of the bridge and the resistors R_9–R_{10} and R_7–R_8 the other two arms. Balance is determined by a microammeter connected across the bridge R_7–R_9. The difficulty of matching has been minimized by the use of the 6A6, since its two triode sections were manufactured at the same time and operate in the same environment.

While a certain degree of stability is attained by the use of the matched triodes in the bridge circuit, the stability of the device has been further increased by placing the two sections of the tube in individually balanced mu-balance circuits (*2*, *8*). The ratio of the resistance R_6 to the effective resistance of the network R_5–R_3–R_{12}–R_4 is chosen to be slightly higher than the amplification factor (manufacturer's specifications) of the tube, so that individual adjustments to compensate for slight differences in the two sections can be made by adjusting the resistors R_3 and R_4.

Batteries B_1 and B_2 are introduced to increase the sensitivity by opposing the high negative grid potentials which would normally result from the mu-balance network (*8*). These batteries are small, since there is no current drained from them.

The apparently complex switching arrangement adapts the instrument to a variety of purposes.

The power supply is designed with an 84-type rectifier and appropriate filter system to permit operation on alternating and direct current.

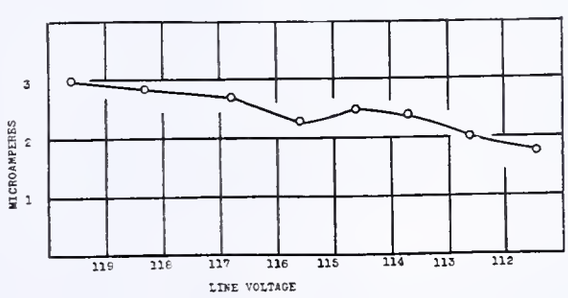

FIGURE 2. STABILITY CURVE

Operation

The proper operating condition may be determined by performing the following operations:

Open S_1; throw S_2 to the right and S_3 to the left; S_4 should be closed. Disconnect the microammeter from the circuit by removing the "jumper" across binding posts P_1 and P_2 and connect a 0–2 milliammeter between R_9 and R_{10}. Adjust resistor R_4 until the change in plate current with change in line voltage becomes a minimum. Changes in line voltage can be most easily secured by placing a variable resistance in series with the

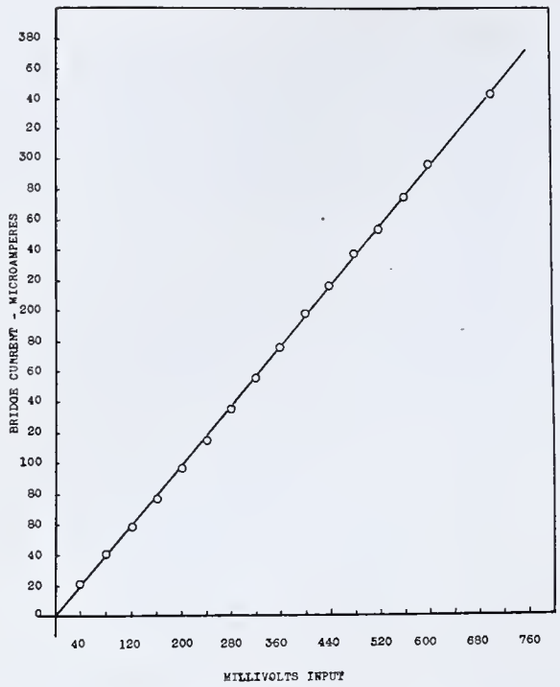

FIGURE 3. SENSITIVITY CURVE

line. The same operation should now be repeated with the other section of the tube. For very high stability readjustment of R_4 may now be necessary. The operating stability may be judged by reconnecting the microammeter and noting the change in its reading with line voltage. Improvement in stability can often be obtained by further critical readjustment of R_3 and R_4 until maximum stability is indicated by the microammeter. Once this adjustment is completed, no further changes are required until replacement of the tube is made.

Before using the instrument, the microammeter should be made to read zero, with zero input, by adjusting resistors R_7 and R_9. This compensates for differences in the plate impedances of the two sections of the tube.

The switching arrangement permits the voltmeter to be used in the following ways:

1. S_1 open, S_2 to the right, S_3 to the left, S_4 closed.
The instrument is now a high resistance voltmeter with a range 0 to 1 volt.
2. S_1 open, S_2 to the right, S_3 to the left, S_4 open.
These operations disconnect the grid leak and make the instrument available for electrometric titrations and other potential measurements where low current drain is important. Under these conditions the maximum current will be 10^{-8} ampere.
3. S_1 closed, S_2 to the left, S_3 to the right, S_4 any position.
Under these conditions the instrument serves as a galvanometer which may be used in the usual Poggendorf method. When balanced, the meter will show equal deflections when S_2 is moved from left to right. When the external electrode resistance is high, S_1 should be left open. It should be noted that the second section of S_2 serves to disconnect the microammeter during the transition of the first section of S_2, thus preventing the meter from reading off-scale during the interval the grid is open.

Stability and Sensitivity

The degree of stability that is obtained is shown in Figure 2. The variation produced by ordinary changes in line-voltage will produce imperceptible changes on the 0–200 microammeter recommended.

The sensitivity curve, Figure 3, shows that the microammeter readings are linear with input voltage and that a 0–200 microammeter provides ample range for all electrometric titrations.

Summary

A self-contained vacuum-tube voltmeter is described which is capable of operating on alternating and direct current lines and designed to minimize the effects of line-voltage variations. It is adaptable to a variety of uses where low voltages are to be measured with a minimum current drain.

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A Simple Rotating Ball Mill

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FOR certain investigations it was necessary to design a simple, compact, efficient, and portable ball mill. Several modifications were tried, of which the mill described below has proved the most satisfactory. It consists of two horizontal rotating shafts upon which is placed a cylindrical container made of steel or glass, holding the material to be pulverized, and rotated by the revolving shafts. The mill

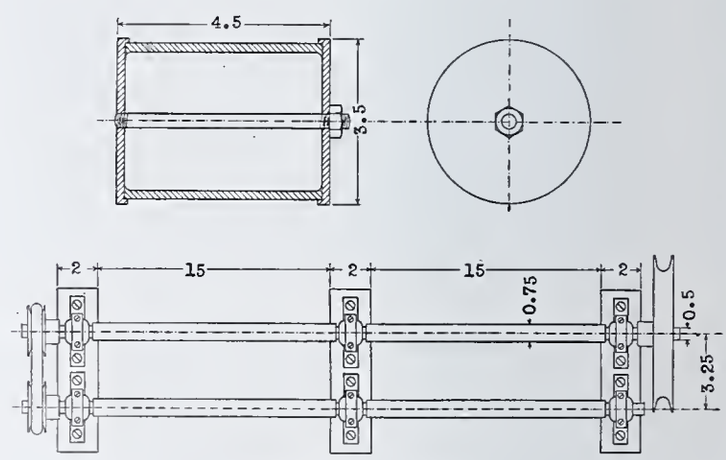

FIGURE 1. DIAGRAM

Upper left, cross section of container. Upper right, end view of container. Lower, top view of rotating shaft assembly.

may be easily constructed at a small cost in the average laboratory. Many substances, such as soils, pure minerals, plant materials, bacteria, glass, etc., have been ground in this mill.

Figure 1 gives a general idea of the principles of this mill The shafts are steel, 0.5 inch by 3 feet or longer and are 3.25 inches apart from the center of each shaft. The bearings are common, split pillow blocks with a hole drilled through the top for oiling purposes. The shafts between the bearings are covered with ordinary rubber tubing which is slipped on with the aid of powdered talc. The rubber tubing quiets the operation and gives better traction to the mill. There is a 2-inch pulley at one end of each shaft, connected by a 0.25-inch round belt. The other end of one shaft has a larger pulley, approximately 4 to 6 inches in diameter, connected to an electric motor of about 0.25 horsepower by an endless belt.

The grinding chamber is made of a steel tube 3.25 inches in diameter by 3.75 inches long, machined on the inside and ends, as illustrated. The ends are steel plates 3.5 inches in diameter by 0.25 inch thick, turned and grooved to fit the chamber. A hole was drilled and threaded in the center of one plate to fit a 0.375- by 4.5-inch steel rod threaded at both ends. The center of the other plate was drilled with a slightly larger hole. A nut was screwed on the outside of the rod, which runs through the center of the chamber, tightening the two plates against the turned steel tube. The plates and steel tube should be machined carefully; otherwise the mill will not retain finely divided material. These specifications do not have to be closely adhered to, but may be varied as needed.

The rate of grinding and the degree of subdivision depend upon the interrelation of the amount of material inserted, the size and speed of mill, and the number, size, and weight of balls employed. It was found that 0.75-inch steel ball bearings were most generally efficient.

Depending upon the materials ground and requirements conditioned by the investigation (freedom from impurities abraded during the process, etc.) the type of chamber may be modified. In certain cases, ordinary rubber or cork-stoppered round bottles, from 3 to 5 inches in diameter, with glass marbles about 0.75 inch in diameter, were used advantageously, as in the pulverizing of bacteria, sugars, and plant materials. Uniform mixtures of soil or semi-plastic suspensions have been produced by subjecting the material to the rolling process in bottles, without the aid of marbles or balls.

When larger scale methods are advantageous, a series of roller units may be constructed one upon the other, connected to a single motor.

Acknowledgments

The writer wishes to express his thanks to members of the staff of the Division of Plant Nutrition and to V. Arntzen of the Department of Engineering for suggestions given.

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Constituents of Pyrethrum Flowers

Determination of Pyrethrin II

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SINCE the isolation and characterization by Staudinger and Ruzicka (*10*) of the insecticidal constituents of pyrethrum flowers, pyrethrin I and pyrethrin II, nine methods have been proposed for their quantitative determination. Three of these methods determine pyrethrin I and pyrethrin II separately; the other six determine the total pyrethrin content.

Staudinger and Harder (*9*) were the first to propose a method for determining the pyrethrins separately. Their method, known as the acid method, is based upon the fact that both the pyrethrins are esters and that on hydrolysis pyrethrin I yields a monocarboxylic acid volatile with steam, whereas pyrethrin II yields a dicarboxylic acid which is nonvolatile. The methods of Tattersfield, Hobson, and Gimingham (*11*) and of Seil (*8*) are modifications and improvements of the original Staudinger and Harder method. Of the three procedures, that of Seil is the most rapid, and is probably the most satisfactory. All three methods tend to give high results because of the presence of fatty acids, which are known to be present in pyrethrum extracts both in the free state and in combination as esters or glycerides (*7*).

If the two pyrethrins were equally toxic to insects, it would be immaterial which method of analysis was used, but most tests indicate that pyrethrin I is more toxic than pyrethrin II. Determination of the individual pyrethrins, therefore, may give a more accurate insecticidal value of pyrethrum flowers than a determination of the total pyrethrins.

It is well known that most methyl esters yield methyl iodide quantitatively on refluxing in constant-boiling hydriodic acid (*5*, *6*). The method proposed in this paper is based upon the fact that pure pyrethrin II, being a methyl ester, yields, on refluxing with hydriodic acid, the quantity of methyl iodide required by its formula (*4*). The latter is determined by the volumetric method of Vieböck and Schwappach as modified by Clark (*3*). In this method the methyl iodide is absorbed in an acetic acid solution of potassium acetate to which bromine has been added. The following reaction then takes place:

$$CH_3I + Br_2 \longrightarrow CH_3Br + IBr$$
$$IBr + 2Br_2 + 3H_2O \longrightarrow HIO_3 + 5HBr$$

The solution containing the iodic acid is treated with formic acid to remove the excess bromine, potassium iodide is added, the solution is acidified with dilute sulfuric acid, and the liberated iodine is titrated with a standard sodium thiosulfate solution. As 6 atoms of iodine are liberated for each mole of methoxyl (OCH_3), 1 cc. of 0.05 *N* sodium thiosulfate is equivalent to 3.11 mg. of pyrethrin II. It thus follows that, for pyrethrum flowers containing about 1 per cent of pyrethrins, a 5-gram sample is ample for a macrodetermination.

The determinations were made in the apparatus described by Clark (*2*).

Reagents

The following reagents, all of analytical grade, were used in the determinations, and it was considered essential to determine the blank on them:

Petroleum ether (b. p. 30° to 60° C.)
Chloroform
Phenol
Hydriodic acid, sp. gr. 1.70, constant-boiling, which has been treated with hypophosphorous acid to remove the free iodine. (The hydriodic acid furnished by Merck & Co. has been treated with hypophosphorous acid.) In order to reduce the blank, it is desirable to pass a stream of carbon dioxide through the boiling solution under reflux for 2 or 3 hours.
Potassium acetate solution, 20 grams dissolved in 200 cc. of glacial acetic acid
Sodium acetate solution, 25 grams dissolved in 100 cc. of water
Bromine
Formic acid (at least 90 per cent purity)
Sulfuric acid solution, 10 cc. dissolved in 100 cc. of water
Potassium iodide
Sodium thiosulfate solution, 0.05 *N*

Procedure

Preparation of Extract. A 5-gram sample of finely ground pyrethrum flowers was extracted for 7 hours with petroleum

ether (b. p. 30° to 60° C.) either in a Soxhlet or in a Butt extractor (*1*). For the Soxhlet extraction a 100-cc. extractor fitted with an extra-length condenser was used. The Butt extractor used was 18 cm. long and 2.5 cm. in diameter. It was fitted with an Allihn condenser and provided with a ground-glass joint in order that the same flask might be used for the extraction and the methoxyl determinations, making the transfer from one flask to another unnecessary.

The sample for the Soxhlet extractor was handled in the usual manner; that for the Butt extractor was wrapped in filter paper (*12*).

Pyrethrin II Determination. After the extraction most of the solvent was removed by heating in a water bath at 70° C. When the extract was prepared in the Soxhlet extractor, the residue was quantitatively transferred to the flask used for the methoxyl determination by means of 20 cc. of chloroform used in small portions. A small boiling rod was then placed in the flask and the chloroform was removed by heating in a water bath, the last traces being removed under reduced pressure.

Two and one-half cubic centimeters of melted analytical-quality phenol and 5 cc. of constant-boiling hydriodic acid were added, and the flask was connected with the remainder of the apparatus. The absorption tubes contained 10 cc. of potassium acetate solution, to which 20 drops of bromine had been added. Unless a large excess of bromine is used, low results are obtained.

The mixture in the flask was boiled at such a rate that the vapors did not rise more than half the length of the condenser, and at the same time a slow stream of carbon dioxide was passed through the flask.

After 1.5 hours the boiling was discontinued, and the contents of the absorption tubes were washed into a flask containing 5 cc. of sodium acetate solution. The volume of liquid was adjusted to about 125 cc., and 20 drops of 90 per cent formic acid were added to remove the excess bromine. When the liquid had become water-white and the last traces of bromine had been removed, 2 cc. of dilute sulfuric acid were added, followed by 1 gram of potassium iodide. The free iodine thus liberated was titrated with a 0.05 *N* solution of sodium thiosulfate, 1 cc. of which is equivalent to 3.11 mg. of pyrethrin II. It thus follows that, for a 5-gram sample:

$$\text{Cc. of } 0.05\ N \text{ sodium thiosulfate} \times 0.0623 = \text{per cent pyrethrin II}$$

Results

Table I shows results obtained by the proposed method as compared with values found by the Tattersfield, Hobson, and Gimingham method and the Seil method.

In all cases the values obtained by the proposed method are somewhat lower than those obtained by the other two methods. The greatest difference occurs in powder No. 1934–4, although larger samples (10 grams) and longer periods of extraction (10 to 18 hours) were used. As the presence of free fatty acids, esters, and glycerides in the flowers tends to give high results with the acid methods, the values obtained by the methoxyl method probably more nearly represent the true pyrethrin II content.

Since variation in the time of boiling from 1 to 2 hours made little difference in the results, 1.5 hours was adopted as the recommended procedure.

If pyrethrum flowers contained appreciable quantities of methyl pyrethrolone, as is claimed by Ripert (*7*), the results obtained by the methoxyl method would be significantly higher than the values obtained by the acid methods, since methyl pyrethrolone is soluble in petroleum ether and has a methoxyl content about twice that of pyrethrin II.

The results obtained on extracts made in a Butt-type extractor are about the same as those obtained on extracts prepared with a Soxhlet extractor. The Butt extractor has the advantage of requiring less solvent for extraction and also of eliminating the necessity of transferring the extract from the extraction flask to the methoxyl flask.

Pyrethrum powder No. 10 is about 10 years old. The analyses obtained by the acid methods were made in December, 1934, and those by the methoxyl method in February, 1935.

Table I. Values for Pyrethrin II Obtained by the Methoxyl Method, as Compared with Values Obtained by the Acid Methods

Powder No.	Type of Extractor	Time of Boiling in Methoxyl Detn.	Pyrethrin II Found: Methoxyl method	Tattersfield method	Seil method
		Hours	%	%	%
1932–1	Butt	2.0	0.38	0.48	0.42
	Butt	2.0	0.38	0.42	0.42
	Butt	1.25	0.37	....	....
	Butt	1.25	0.37	....	....
	Butt	1.25	0.37	....	....
	Soxhlet	1.25	0.39	....	....
	Soxhlet	1.25	0.39	....	....
	Soxhlet	1.25	0.37	....	....
1934–1	Butt	1.75	0.33	0.43	0.40
	Butt	1.75	0.34	0.42	0.39
	Butt	1.75	0.34	0.43	....
	Soxhlet	1.5	0.36	....	....
	Soxhlet	1.5	0.34	....	....
1934–2[a]	Soxhlet	1.5	0.25	0.30	0.28
	Soxhlet	1.5	0.23	0.29	0.30
1934–3	Soxhlet	1.5	0.37	0.52	0.47
	Soxhlet	1.5	0.37	0.53	0.47
1934–4[b]	Soxhlet	1.0	0.35	0.47	0.54
	Soxhlet	1.0	0.37	0.47	0.54
	Soxhlet	1.0	0.36	0.48	....
	Soxhlet	1.5	0.39	....	....
	Soxhlet	1.5	0.36	....	....
	Soxhlet	1.5	0.38	....	....
10	Butt	1.0	0.22	0.28	0.32
	Butt	1.0	0.22	0.28	0.33
	Soxhlet	1.0	0.23	....	....
	Soxhlet	1.0	0.23	....	....
Russian Roseum	Soxhlet	1.5	0.11	0.14	....
	Soxhlet	1.5	0.11	0.14	....

[a] Time of extraction 8 hours.
[b] 10-gram samples were used and the time of extraction ranged from 10 to 18 hours.

Summary

A rapid method for the determination of pyrethrin II, based on the fact that pyrethrin II yields methyl iodide when boiled with hydriodic acid, is proposed. The methyl iodide is determined volumetrically by converting it into iodic acid and titrating with sodium thiosulfate the iodine liberated on addition of potassium iodide.

A comparison of the results obtained by the proposed method with values obtained by the acid methods shows that in all cases the new method gave values somewhat lower than the acid methods.

Acknowledgment

The writers wish to express their appreciation to J. J. T. Graham, of the Food and Drug Administration, U. S. Department of Agriculture, for supplying the samples of pyrethrum powders and the results that he obtained by the acid methods.

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A Rapid Precision Viscometer

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The accuracy of the Saybolt viscometer is compared on a theoretical basis with viscometers whose efflux time is linear with viscosity. Possible errors resulting from the use of Saybolt data to obtain the viscosity index of light oils are discussed.

The Ubbelohde capillary viscometer is modified by the use of dual capillaries and by mounting the whole in a vapor bath. Thus greater operating speed is obtained than is afforded by the Saybolt instrument, along with the high inherent accuracy of capillary viscometers.

During recent years the great importance of the viscosity index as a property of motor oils has come to be generally recognized. It was soon realized in many laboratories that the Saybolt instrument did not furnish results of high enough precision to distinguish between oils differing by two or three viscosity index units (Dean and Davis, *3*) or even ten units in the case of very light oils.

Accordingly, attempts were made to improve on the viscosity index system by such methods as that of Larson and Schwaderer (*6*) where the spread between a Coastal and a Pennsylvania oil was divided into 8 instead of 100 parts. However, the advent of solvent extraction brought out the desirability of detecting small changes in viscosity index as a method of evaluating various solvent extraction processes, following the change in viscosity index from stage to stage, and studying the effect of various treating agents, and the addition of pour-point depressors, wax, and other substances to oils. Therefore, many laboratories adopted Ostwald viscometers in one form or another.

Comparison of Errors of Saybolt and Long Capillary Tube Instruments

Figure 1 shows the error in viscosity index units resulting from a 1 per cent error in the efflux time of a 100 viscosity index oil in a capillary viscometer, compared to that of the short-tube Saybolt with its high kinetic energy correction. It is to be noted that when the error in the capillary type is of the same amount and in the same direction at both 37.78° and 98.89° C. (100° and at 210° F.), a greater compensating effect results in the case of the capillary viscometer than in the case of the Saybolt instrument. This is the type of error most likely to result from the calibration of the tubes, either Saybolt or capillary.

Table I. Effect of 0.4-Second Timing Error on Viscosity and Viscosity Index

	Efflux Time		Kinematic Viscosity in Centistokes		Saybolt Equivalent of Observed Kinematic Viscosity	Viscosity Index	
	True	Observed	True	Observed		True	Observed
Saybolt	40.0	40.4	4.165	4.304	40.40	100	114.9
Capillary	40.0	40.4	4.165	4.208	40.12	100	105.3
Capillary	120.0	120.4	4.165	4.179	40.04	100	101.5

According to Ellis (*4*) the inherent accuracy of a stop watch which has a balance wheel beat of 0.2 second is about 0.4 second—that is, two mechanically perfect watches might vary by that amount. In Table I this is interpreted in terms of an oil of 40 seconds Saybolt. The belief of many that the sole advantage of capillary-type instruments lies in the fact that long efflux times are involved is shown by Table I to be incorrect, since the efflux time of the oil on both Saybolt and capillary viscometers is taken as 40 seconds, and yet the error in viscosity index is reduced to little more than a third in the latter instrument. However, since actual efflux times are usually a small fraction of the entire time required for a viscosity determination on such light oils, it is convenient to use a smaller bore tube and obtain efflux times at least 3 times as long, which gives a degree of accuracy as shown in the third row, Table I.

The use of electric stop clocks may also lead to errors due to frequency variations. The fact that a telechron clock keeps excellent time does not protect against variations over the short period required for a viscosity measurement. The Chicago system which involves Illinois, Wisconsin, Indiana, and parts of Ohio often has deviations of 0.2 per cent with occasional variations even greater. Small local systems may have variations up to 1 per cent.

A third source of error in Saybolt measurements is the variation from tube to tube. A standard tube is one with dimensions within certain tolerances which is calibrated at the Bureau of Standards on one oil with an approximate viscosity of 181 seconds. However, differences in diameter and length of tube might compensate to give identical results on such an oil in two tubes which might differ appreciably on lighter oils.

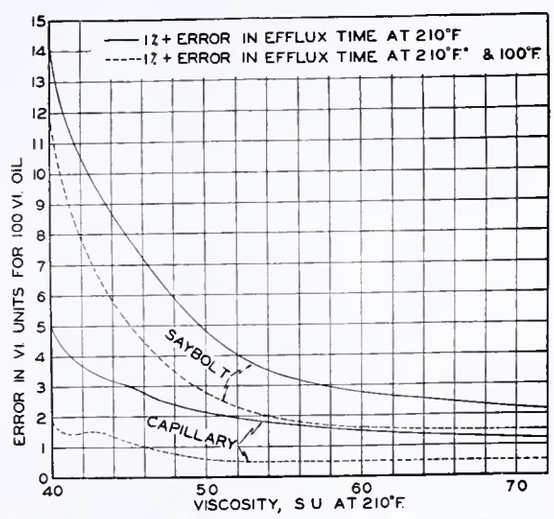

Figure 1. Comparison of Viscometer Errors

A fourth source of error arises from the fact that the values obtained on the same Saybolt instrument vary slightly with the type of bath, bath liquid used, and method of stirring the oil. This is in some measure due to the fact that a temperature gradient exists in the oil in the Saybolt instrument, the bath liquid giving up heat to the oil and the oil dissipating heat at the surface and at the orifice.

The Saybolt tube is defined by the master tube at the Bureau of Standards. Thus a change in the standard from time to time is possible. Also, the method of standardizing tubes against the master at one value only has resulted in a multitude of conversion tables from Saybolt to kinematic viscosity, all probably correct for the tube used and the operator.

The best solution, provided the Saybolt viscosity is to be retained, would seem to be to define the Saybolt by its re-

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lationship to kinematic viscosity. Then each individual could calibrate his tube and plot a deviation chart, much as we use standard thermocouple tables.

Suspended-Level Instrument

For several years accurate viscosity measurements in this laboratory had been carried out in the British Engineering Standards Association (*1*) type of Ostwald viscometers. Determinations were slow and tedious, however, and the use of the instrument was confined to a few research problems. In 1933 Ubbelohde (*8*) published an account of his suspended-level viscometer, which had such obvious advantages that it was adopted by this laboratory, using a vapor bath for temperature control. Several changes have since been made, the result being an apparatus that excels the Saybolt not only in accuracy but also in speed and simplicity of operation.

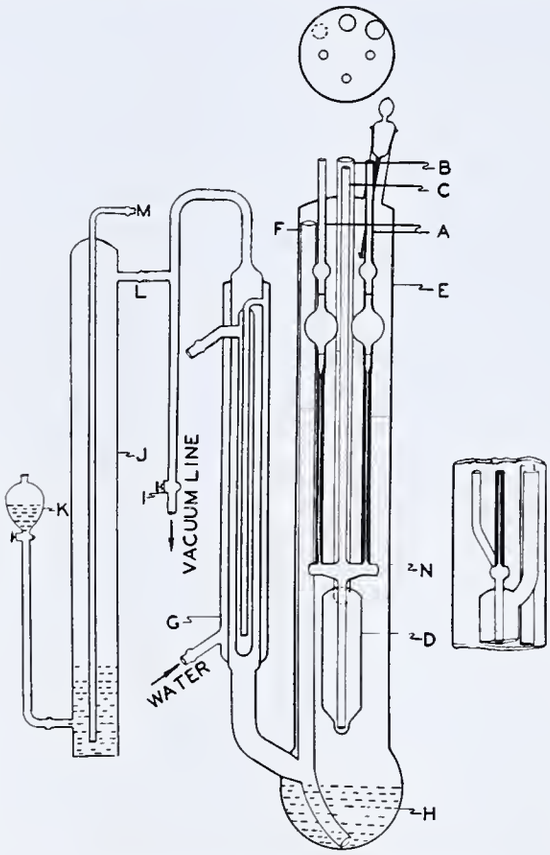

FIGURE 2. DIAGRAM OF APPARATUS

The apparatus, shown in Figure 2, consists of two capillaries of different sizes, *A*, sealed into a vapor bath, *E*. Tube *C* is an air vent for producing the suspended level and tube *B* is connected to the oil reservoir, *D*.

The bulb is filled with a pure organic liquid with a normal boiling point slightly above the temperature at which it is desired to operate the viscometer, methylene chloride being suitable for use at 37.78° C. (100° F.) and tertiary amyl alcohol for use at 98.89° C. (210° F.). Vacuum is turned on and regulated by valve *I* to obtain a slow rise of bubbles up column *J*. The bulb, *H*, is heated electrically, causing vapor to rise up the jacket and down the riser, *F*, to the condenser, *G*, and return as liquid to the bulb, *H*. To obtain exactly the desired temperature, the pressure is adjusted by adding or removing water from the pressure-regulating column, *J*, by means of the leveling bottle, *K*. By changing the connection to the column from tube *L* to tube *M* and substituting an air line for the vacuum line, the viscometer can be operated under pressure; this is occasionally necessary on days of low barometer.

Procedure

Oil is poured through a 100-mesh filter down tube *B* until reservoir *D* is about one-half full; this requires about 12 cc. After a short wait of 1 or 2 minutes to allow the oil to reach bath temperature, tube *C* and the smaller capillary, *A*, are closed off with the fingers and oil is drawn up into the right capillary by suction well above the upper mark. The suction line and fingers are then removed, establishing the suspended level at *N*, and the time for the oil to pass between the marks is noted. If the time is less than 100 seconds the oil is immediately drawn up into the smaller (left) tube and the efflux time observed. The kinematic viscosity is obtained by multiplying the efflux time by a factor, determined by calibrating each tube of the instrument on an oil of known viscosity. At short efflux times a kinetic energy correction is necessary, which is always less than 1 per cent for motor oils. The kinetic energy correction is calculated from the dimensions of the instrument.

The oil is quickly removed through tube *C* by a suction line connected to a trap. The instrument is flushed with a narrow cut naphtha with an initial slightly above the bath temperature. The naphtha is also removed by suction through tube *C* and the instrument sucked dry. The entire cleaning operation requires about one minute.

Calibration

The equation for all capillary type of viscometers can be expressed by the relation

$$v = \frac{\pi g h r^4}{8lV} t - \frac{mV}{8\pi l t}$$

where r = radius of capillary in cm.
v = kinematic viscosity in centistokes
t = efflux time in seconds
g = gravity constant in cm. per second per second
h = average effective head in cm.
l = length of capillary in cm.
V = volume in cc.
m = coefficient in kinetic energy term

The kinetic energy term was evaluated from dimensions of the instrument, where $m = 0.8$ (*9*), $V = 3.75$ cc., and $l = 12$ cm. Thus the equation could be simplified into the form

$$v = C_1 t - \frac{C_2}{t}$$

Since the dimensions have been chosen so that $C_2 = 1$, the correction in centistokes is merely the reciprocal of the efflux time and is easily applied. This correction term, however, is negligible for efflux times in excess of 100 seconds except in the case of the smallest capillary size.

The coefficient C_1 is easily evaluated by the use of an oil of known viscosity.

Results

Two instruments were installed in an inspection laboratory and a short period of instruction given to four non-technical operators (A, B, C, and D). They were furnished 14 samples of various brands of Pennsylvania grade motor oils which had been inspected some months previously on Ostwald viscometers. The result of the survey is shown in Table II. These operators were accustomed to read the stop watches to even seconds only, and this procedure was not varied, as the watches were in poor condition. The results were reported in Saybolt seconds obtained from tables converting directly from efflux times. This table does not show the greatest degree of accuracy obtainable, but does show the freedom of the instrument from the personal equation under the most unfavorable conditions. In Table III is shown the agreement that can be obtained with other types of viscometers in other laboratories.

Advantages

The advantages in the use of the vapor-bath suspended-level viscometer are:

SPEED. The viscometer equals the Saybolt in speed on light oils but is considerably faster on heavy oils. This speed is due to five factors, (1) the vapor bath affords nearly instantaneous heating, (2) a short cleaning cycle, (3) no necessity to weigh or measure the amount of oil charged, (4) no

Table II. Equivalent Saybolt Viscosities Using Vapor Bath Suspended-Level Viscometer

Oil	Temp. ° F.	Vapor Bath Suspended-Level Viscometer A	B	C	D	Ostwald
1	100	160	160	160[a]	160	158.9
	210	43.3	43.3	43.3[a]	43.3	43.3
		(89)[b]	(89)	(89)	(89)	(86)
2	100	218.5	218.5[a]	218	218[a]	218.2
	210	47.5	47.5[a]	47.5	47.5[a]	47.4
		(96)	(96)	(96)	(96)	(95)
3	100	194.5	192.5[a]	194	194[a]	...
	210	45.6	45.6[a]	45.6	45.6[a]	...
		(101.5)	(102.5)	(101.5)	(101.5)	...
4	210	46.6	46.6[a]	46.6[a]	46.7[a]	...
5	100	188	...	188[a]	...	184.2
	210	45.4	45.4[a]	45.4	45.4[a]	45.3
		(94)	...	(94)	...	(96)
6	210	50.2	50.2[a]	50.3[a]	50.2t	50.2
7	100	257.5	256[a]	255[a]	256[a]	254.5
	210	50.2	50.2[a]	50.2[a]	50.2[a]	50.1
		(101)	(102)	(102)	(102)	(102.5)
8	100	304	302.5[a]	304[a]	305[a]	300
	210	52.6	52.6[a]	52.6[a]	52.6[a]	52.3
		(97)	(98)	(97)	(97)	(97)
9	100	287	286	287[a]	287[a]	284
	210	51.4	51.4	51.4[a]	51.4[a]	51.2
		95.5	(95.5)	(95.5)	(95.5)	(95.5)
10	100	374.5	375	374	376	372.5
	210	57.5	57.5	57.5	57.5	57.3
		(102.5)	(102.5)	(102.5)	(102)	(102.5)
11	100	391.5	391	390[a]	388[a]	388.4
	210	59.2	59.1	59.3[a]	59.2[a]	59.0
		(106)	(105.5)	(107)	(107)	(106)
12	100	348[a]	345	342[a]	344[a]	342.3
	210	54.9[a]	54.8	55.0[a]	54.9[a]	54.8
		(96.5)	(96)	(98.5)	(97)	(97.5)
13	100	492[a]	493[a]	495[a]	492[a]	...
	210	63.7[a]	63.6[a]	63.6[a]	63.7[a]	...
		(99)	(99)	(99)	(99)	...
14	100	531.5[a]	531[a]	530[a]	531[a]	...
	210	67.7[a]	67.6[a]	67.8[a]	67.7[a]	...
		(104)	(104)	(104)	(104)	...

[a] Values based on single determinations only.
[b] Values in parentheses are Davis, Lapeyrouse, and Dean viscosity indices (*2*).

Table III. Viscosity of Oil 15

Laboratory	Viscometer	Kinematic Viscosity in Centistokes 100° F. (37.78° C.)	210° F. (98.89° C.)	Saybolt Equivalent from A. S. T. M. Equations 100° F. (37.78° C.)	210° F. (98.89° C.)
Bureau of Standards	Bingham	34.8	5.31	162	43.4
Laboratory 1	Ostwald	34.78	5.328	161.9	43.44
Laboratory 1	Ubbelohde Suspended-level	34.85	...	162.2	...
Laboratory 1	Vapor-bath suspended-level	34.87	5.325	162.3	43.43
Laboratory 2	Modified Ubbelohde	34.95	5.32	162.6	43.4
Laboratory 3 (inspection)	Vapor-bath suspended-level	...	...	162	43.4

cleaning or recharging to obtain check determinations, and (5) the use of dual capillaries keeps all efflux times between 100 and 600 seconds. In practice, about 40 oils can be inspected at two temperatures in one day by one operator using two instruments. This includes check determinations or a total of 160 viscosities.

Accuracy. The degree of accuracy at present is limited by the viscosity standards available. Checks on the same instrument to better than 0.1 per cent are attainable.

Simplicity. Viscosities at 37.78° and 98.89° C. (100° and 210° F.) are sufficient for most practical purposes. The 54.44° C. (130° F.) Saybolt inspection is used chiefly on oils whose times of flow at 100° F. would be unnecessarily long. With the vapor bath suspended-level instrument the heaviest bright stocks can be examined at 100° F. as quickly and easily as light oils.

Small Sample. Only about 12 cc. of oil are required for a determination.

Visibility. Excellent visibility is afforded at all times. This is a decided improvement, especially at 210° F., as in localities of low barometric pressure, where an oil bath must be used, with Ostwald viscometers, visibility is poor.

Freedom from Alignment Errors. The instrument has the same low sensitivity to alignment errors as the offset type Ostwald of Grüneisen (*5*) and later of Willihnganz, McCluer, Fenske, and McGrew (*10*).

Drainage Errors. Drainage errors are negligible on oils. They are of two types in Ostwald viscometers:

Drainage in the lower bulb results from varying amounts of oil adhering to the walls and thereby altering the effective liquid head. In a given instrument, it is dependent upon the viscosity of the oil and the rate at which the oil is drawn up into the upper bulb. This error is completely avoided in the suspended-level type of instrument.

Drainage in the upper bulb, unlike lower bulb drainage, affects the volume term in Poiseuille's equation rather than the height. Hence, in certain instances these two errors may nearly offset each other. According to McCluer and Fenske (*7*), the drainage should be determined by the use of an auxiliary bulb of the same size and shape as the upper bulb. This can be done by a procedure of weighing the auxiliary bulb both dry and after a determination. However, in the case of similar liquids such as petroleum oils the possible error is negligible, as the volume remaining is proportional to the efflux time. Since in a given instrument the efflux time varies directly as the viscosity, the drainage is a constant which is taken care of if the instrument is calibrated on similar liquids.

Rapid Operation. Continuous operation is unnecessary, as the viscometer can be brought up to temperature in about 3 minutes.

Saving in Space. Each instrument requires about a square foot of desk space.

Cost. The instrument is relatively inexpensive, as no thermostat, relays, stirrers, rheostats, or thermoregulators are required.

Retention of Original Calibration. Two instruments in daily use for nearly a year have shown no detectable deviation from the original calibration.

Disadvantages

Fragility. The instrument, being made of glass requires care in handling. However, no breakages have been encountered so far even in the hands of nontechnical operators.

Necessity for Applying a Factor to Result. It is necessary to apply a factor, determined for each instrument, to the results. However, by the use of precision capillary tubing and careful dimensioning, any predetermined factor may be obtained, thus allowing a standardization of the viscometer. In the original Ubbelohde (*8*) viscometer it is the custom to make the factor a power of ten by suitable dimensioning.

Clogging of Capillary. In the smaller capillary sizes, care is necessary to screen out all solids. A metal screen is used, as fibers from cloth and paper filters are troublesome if allowed to get into the tubes.

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Determination of Water

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IN THE determination of water one of the following methods is usually applied: (1) the sample is dried and the water content calculated from the loss in weight; (2) the sample is dried in a stream of dry gas, the gas stream is passed through a weighed water absorbent—for example, anhydrous calcium chloride—and the increase in weight of the latter is calculated as water; (3) the sample in a distilling flask is mixed up with a liquid that boils above 100° C. and is immiscible with water—for example, xylene—then the mixture is distilled, the distillate being received in a graduated vessel from which the distilled-over water is read off directly (Marcusson procedure). All three methods have both advantages and drawbacks. The following procedure is an extension of the distillation method, and it has the advantage in that small quantities of water can be determined accurately, even when the material contains only a few tenths per cent of water.

Procedure

Briefly the method involves (1) distillation of the material with xylene or toluene, (2) dehydration of the distillate with a weighed quantity of anhydrous copper sulfate, filtration, and washing of the copper sulfate with benzene and ether with subsequent drying *in vacuo*, and (3) calculation of water from the increase in weight of the copper sulfate. The determination is carried out as follows:

A weighed sample of 0.5 to 500 grams, depending upon the expected water content, is mixed with 100 to 200 ml. of xylene in a distilling flask. The flask is connected with a straight (Liebig) condenser and the distillate is caught in an Erlenmeyer flask provided with a glass stopper and containing 0.5 to 5 grams of anhydrous copper sulfate. It is convenient to keep the anhydrous copper sulfate in a weighing glass in a desiccator and to determine the amount introduced into the flask by difference in weight. The distillation should be carried out as rapidly as possible (boiling stone or glass beads) and as much as possible of the xylene should be distilled over. At least 50 cc. of xylene should be distilled off; in some instances xylene is poured back into the distilling flask, taking care to avoid the loss of any copper sulfate thereby—it is more suitable to use fresh xylene—and the distillation then continued. The distillate is shaken well with the copper sulfate in the receiver and filtered by means of a small tube filter.

The filter consists of a tube 10 to 15 mm. in diameter and about 10 cm. long, constricted at the bottom to provide support for a small filter plate on which a filter pad is placed; the filter is washed with ether, dried in a vacuum, and weighed. The xylene distillate is poured through the filter, and all the copper sulfate is brought onto the filter by rinsing the flask with benzene. Then after washing it with ether the filter tube is dried in an evacuated desiccator and weighed. As the liquid runs through the filter very rapidly, some care is required to keep the pad covered with liquid until filtration is complete. If a high vacuum is used, the weighing can be made after 10 to 15 minutes. The increase in weight gives the weight of water.

Rapid drying of the filter can also be accomplished in the following manner:

To a tall glass cylinder, such as is used for taking the gravity of liquids, provided with a two-hole stopper, sulfuric acid is added to a depth of about 5 cm. A capillary tube passes through one hole of the stopper and dips into the acid; the filter is inserted in the other hole and adjusted so that the lower end of the filter tube is preferably 15 to 20 cm. above the acid. The upper end of the filter tube is connected with a suction pump and evacuated. Only a very little air is permitted to enter through the capillary, so that the filter will stand under a vacuum. With this arrangement other precipitates can also be dried quickly at lower temperature. In using this drying device the author finds that it is sufficient to wash the copper sulfate with benzene only, thus dispensing with the frequent use of ether. When a precipitate is dried in this manner, great care must be taken that evacuation does not occur too suddenly; otherwise a part of the precipitate may be carried out with the stream of air. In order to attain rapid and complete drying, it is necessary that only a little air be admitted through the capillary, so that the filter will be under a vacuum.

It is convenient to collect the xylene (toluene), benzene, and ether separately, so that they may again be used as the occasion arises. The ether and benzene must not leave a weighable residue on evaporation to dryness. In contrast with the Marcusson method in which the xylene has to be saturated with water, all liquids must be dehydrated with anhydrous copper sulfate.

The method is applicable to the determination of water in any product which loses its water at 110° to 140° C. and yields no other volatile compounds that act on copper sulfate or are insoluble in benzene and ether. The determination can be carried out either as a macro- or a micromethod.

Table I gives a few determinations of water, and for purposes of comparison includes results obtained by other methods. It will be noted that the results by the two methods are in good agreement. The Marcusson method yields somewhat lower figures than the one described herein, especially when the sample is small. The Hoffman method for the determination of water in starch is very similar to the Marcusson procedure; in place of xylene a mixture of 400 cc. of oil of turpentine and 10 cc. of xylene to 50 grams of starch is used. The water content of materials containing organic solvents—for example, some fatty alcohol sulfonates—cannot be determined by drying, but correct results are obtained by the distillation method. The frothing of fatty alcohol sulfonates and highly sulfonated oils during distillation can be avoided by the addition of dry sodium chloride to the distillation flask.

TABLE I. RESULTS FOR WATER IN VARIOUS ORGANIC PRODUCTS

Material	Method as Described			Comparison Method		
	Sample	$CuSO_4$ Taken	Water Found	Sample	Water Found	Method Used
	Grams	*Grams*	%	*Grams*	%	
Machine oil	500.0	0.0185	0.037	Marcusson method not applicable; oil is dried by heating.		
Crude oil	3.2360	0.1262	3.9	100	3.8	Marcusson
Crude oil emulsion	0.6130	0.5596	91.3	10	90.0	Marcusson
Vehicle grease	4.3685	0.2230	5.1	20	4.5	Marcusson
Machine grease	3.1765	0.0670	1.8	10	[a]	Marcusson
Leather-finishing oil [b]	2.7255	0.0764	2.8	50	2.6	Marcusson
				5.3280	2.95	[d]
Leather-finishing oil [c]	5.6926	0.0968	1.73	4.2620	1.85	[d]
Lardonat X (fatty alcohol sulfonate)	2.3135	1.1465	49.55	15.0	50	Marcusson
				4.6180	53.4	[d]
Starch	0.5615	0.0910	16.2	50	16	Hoffman
				5.0250	16.25	[d]

[a] Not determinable.
[b] Sulfonated neat's-foot oil with 10% neutral oil.
[c] Sulfonated train oil with 40% mineral oil.
[d] Mixed with sand and dried at 105° C.

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Apparatus for the Study of Liquid-Vapor Equilibrium Compositions

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THIS apparatus, originated and used by the authors for the purpose of obtaining samples of liquid and vapor in an equilibrium, is believed to have considerable advantage in speed, simplicity, and convenience over devices used by Othmer (*3*) and Brown (*1*). It checks the published curves for the system alcohol-water, and has been used to good advantage for the design of plant-size fractionating towers.

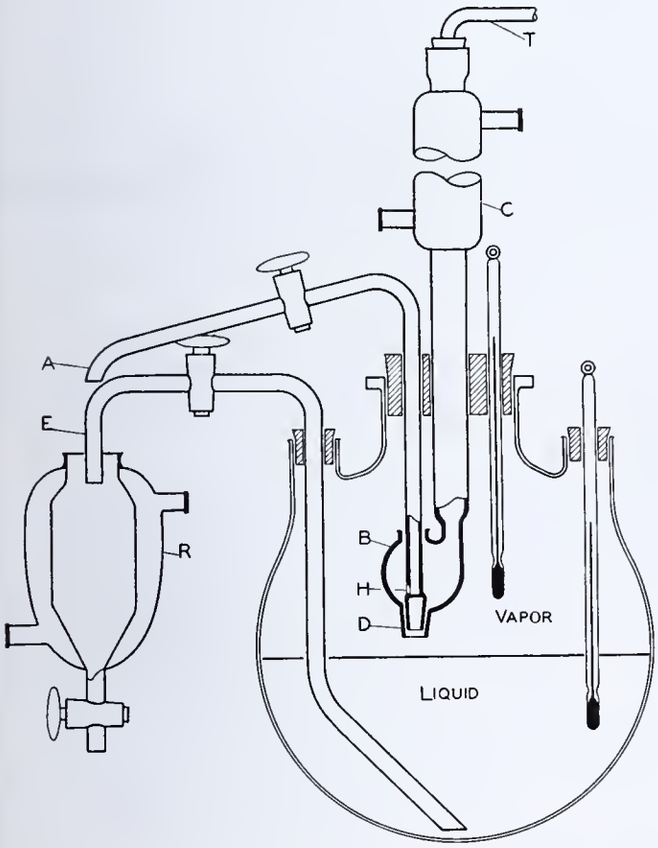

FIGURE 1. APPARATUS ASSEMBLY

Sources of error in the common distilling-flask method, which are eliminated by other methods only at the price of greatly increased complexity of design or slowness of operation, are reduced to a minimum by this method, with little increase in complexity and even greater ease and speed of operation.

The apparatus is shown in Figure 1. The container is a standard 1-liter, three-neck flask, immersed as far as possible in a beaker (not shown) of a transparent heat-transfer fluid, such as glycerol. The cup, *B*, is of glass, about 20 ml. in capacity, with a ground-glass joint, *D*, welded to the bottom. The cup is welded directly to a glass reflux condenser, after fitting the cork as shown. The core of joint *D* is sealed at the bottom and welded to sampling tube *A*. A hole, *H*, is blown in the sample tube immediately above the joint, allowing the sample to pass up through the sampling tube into the cooled receiver, *R*, when the pressure is changed, either by blowing on tube *T* or applying slight suction to the receiver. Samples of the liquid in the flask are taken in the same way through tube *E*. When analyzing samples by the method of specific gravity, the jacketed funnel, *R*, is a convenient means of cooling, so that the samples can be drained directly into a pycnometer, immersed in a constant-temperature bath, and weighed when the temperature reaches the desired point.

To operate, the liquid is boiled gently by heating the bath, using porcelain chips or a capillary air leak to prevent bumping and to keep the liquid in the flask thoroughly stirred. The vapor passes through the top opening of the sample cup to the condenser, and is returned to the cup. The cup is allowed to fill nearly to the top with the joint closed, and the approximate time required is noted. The liquid in the cup is maintained at a constant level by controlling the rate of boiling and leakage through the glass joint. When thermometers and liquid level have remained constant for at least twice as long as is required to fill the sample cup, the samples are taken, and the composition is changed by adding more of one component through the condenser.

Variations in design may be made. A ball-and-seat type joint may be used in place of the regular ground-glass joint and will not break so easily, but is harder to adjust. A small pinhole may be substituted for the adjustable joint, in which case the rate of boiling alone must be controlled to maintain the proper liquid level. If the pinhole-type leak is employed, ground-glass joints may be substituted for the corks, and the apparatus operated under vacuum.

The chief source of error in the apparatus as designed is in the vaporization of the liquid as it leaves the cup and before it becomes completely mixed with the liquid in the flask, but this is small in relation to the total amount of vaporization taking place in the flask. Furthermore, the vapors, thus made relatively too rich in the low-boiling component, tend to be absorbed by the liquid in the flask, thus restoring true equilibrium. No error is incurred from fractionation in the reflux condenser, for regardless of the extent of separation during condensation, the liquid returned to the cup must be identical in composition with the vapor entering the cup. As the cup fills, the composition of the liquid in the flask and of the vapor being boiled off changes somewhat through removal of the low-boiling component, but when steady conditions have been established, the vapor and liquid approach equilibrium, except over the very small area where the reflux from the cup drops back into the boiling liquid.

Care must be exercised in removing the sample from the

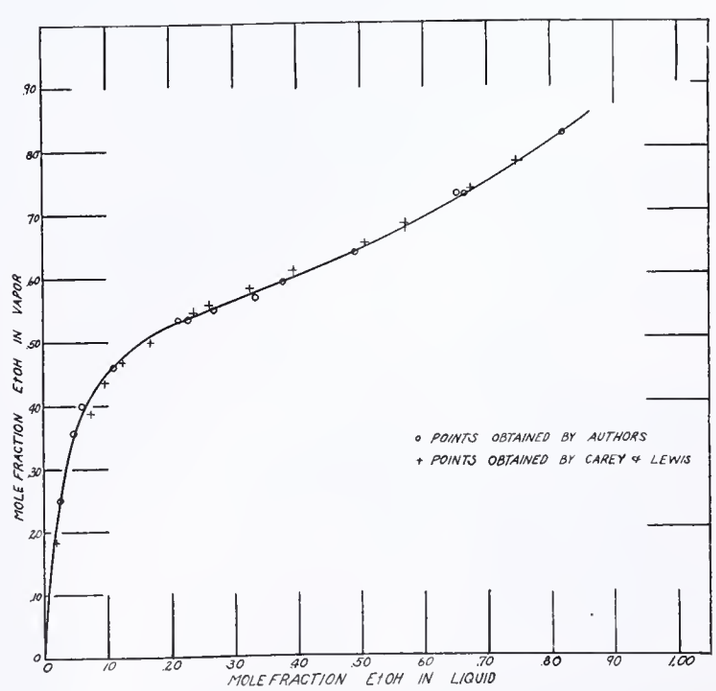

FIGURE 2. LIQUID-VAPOR EQUILIBRIUM CURVE FOR ETHYL ALCOHOL–WATER

cup to avoid contamination of the sample by the hold-up in the reflux. For very careful work, the sample should be removed by applying vacuum to the receiver, rather than pressure to the flask.

TABLE I. LIQUID-VAPOR EQUILIBRIUM DATA FOR ETHYL ALCOHOL–WATER

	Density 25°/25°		Mole Per cent of Ethyl Alcohol	
Run	Liquid	Vapor	Liquid	Vapor
11	0.8083	0.8077	81.8	82.5
12	0.8329	0.8231	66.5	72.8
13	0.8629	0.8365	49.3	64.0
15	0.8839	0.8442	39.3	59.0
17	0.8983	0.8480	33.4	57.0
18	0.9166	0.8516	27.0	55.0
19	0.9169	0.8517	27.0	55.0
20	0.8348	0.8230	65.3	73.5
21	0.8879	0.8437	37.7	59.5
22	0.9301	0.8547	22.7	53.5
25	0.9811	0.8867	4.8	35.7
26	0.9777	0.8820	6.0	40.0
27	0.9635	0.8693	11.0	46.0
28	0.9890	0.9230	2.5	25.0

As a check on the apparatus, the curve shown in Figure 2, was obtained, using ethyl alcohol and water. Samples were analyzed by the method of specific gravity, using a 10-ml. pycnometer in a constant-temperature bath at 25° C., with the tables of the U. S. Bureau of Standards. Samples were drawn by suction on the receiver. Pressure was atmospheric (29.690 inches of mercury).

The data of Carey and Lewis (*2*) are plotted with the authors' in Figure 2 and show good agreement, the authors points being slightly lower than theirs in the middle range, and slightly higher in the lower range.

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The Germanium–Germanium Dioxide Electrode

M. L. NICHOLS AND S. R. COOPER, Department of Chemistry, Cornell University, Ithaca, N. Y.

SINCE the introduction of the hydrogen electrode by Böttger (*1*) in 1897 and its popularization by Hildebrand (*5*) in 1913, potentiometric measurements and titrations have attained great importance. Because of the difficulties of obtaining the highest degree of accuracy with this electrode and its limitations, several electrodes, such as the quinhydrone and many metal–metal oxide electrodes, have been investigated as substitutes (*2, 4, 6*).

In order for a metal to function as a metal–metal oxide electrode it should be slightly soluble, cathodic to hydrogen, and have a slightly soluble oxide. Germanium is a slightly soluble metal, whose dioxide is polymorphic in that it exists in a soluble and insoluble form. Laubengayer and Morton (*8*) state that the insoluble form of the dioxide is not appreciably soluble in 25 *N* hydrofluoric acid, 12 *N* hydrochloric acid, or 36 *N* sulfuric acid, but is 16.8 to 17.8 per cent soluble in 5 *N* sodium hydroxide solution. Since it is also cathodic to hydrogen, this electrode was studied to determine its application to pH determinations and electrometric titrations.

For the electrode

$$Ge/GeO_2, H^+, H_2O$$

the anodic reaction can be represented as

$$Ge(s)2H_2O \longrightarrow GeO_2(s) + 4H^+ + 4F$$

and therefore

$$E_{Ox} = E^m_{Ox} - \frac{RT}{F} \ln [H^+]$$

Then for the cell

$$Ge/GeO_2, HA/\text{salt bridge}/KCl, Hg_2Cl_2/Hg$$

$$E = E_{Ox} - E_{Cal.} \text{ and}$$

$$E^{25°} = E^{m\,25°}_{Ox} - E^{25°}_{Cal.} - 0.0591 \log [H^+] \text{ or}$$

$$E^{25°} = E^{m\,25°}_{Ox} - E^{25°}_{Cal.} + 0.0591 \text{ pH}$$

Therefore the germanium–germanium dioxide should function as a metal–metal oxide electrode with the observed electromotive force for the cell changing 0.0591 volt at 25° C. for each unit change in pH of the solution.

Experimental

The insoluble germanium dioxide was prepared according to the method of Laubengayer and Morton (*8*), and showed practically no solubility in a 48 per cent solution of hydrofluoric acid.

The metallic germanium used had been prepared according to the method of Tressler and Dennis (*10*). The germanium prepared as above was cast into a rod approximately 5 × 5 × 50 mm. A clay boat was filled with an alundum paste and a piece of wood the size of the ingot desired was pressed into the moist paste and the whole dried at 110° C. When the paste had dried, the wood was removed and the depression was filled with powdered germanium. The boat and its contents were heated in an electric combustion furnace at 950° to 1000° C. in an atmosphere of nitrogen, until the metal had melted. The resulting bar of germanium was smoothed with sandpaper. The electrode was mounted in a glass tube with Krönig's cement. The excess of cement was removed with benzene and the electrode was then washed with alcohol and distilled water. The glass tube was filled with mercury to make electrical contact with the metal. An electrode prepared in this manner could be immersed completely in any solution in which it was used.

Pure calomel was prepared from mercury obtained by the electrolysis of mercurous perchlorate (*9*). A saturated calomel electrode was prepared from this pure mercury and calomel. The potassium chloride used was Kahlbaum's "for analysis" which was recrystallized twice from distilled water.

The measurement of the voltage was made with a Leeds and Northrup Type K potentiometer and Type R No. E. galvanometer, shielded with a grounded copper case. The potentiometer was mounted on four rubber stoppers and all wires which were connected to it were either heavily insulated or covered with rubber tubing. A three-cell two-volt storage battery and a Weston standard cell supplied the voltage necessary. The Weston cell was calibrated by the Physics Department of Cornell University and found to give a reading of 1.0184 volts, the value of the last decimal place being uncertain. The solution which was measured and the saturated calomel electrode along with the intermediate vessel were immersed in a thermostat which was regulated at 25° ± 0.05° C.

The electrode was first studied to ascertain if it gave a definite reproducible electromotive force and, if so, the time required for the electrode to come to equilibrium.

TABLE I. TITRATIONS

NaOH	Hydrogen Electrode pH	Hydrogen Electrode E. m. f.	Germanium Electrode, Mechanical Stirring E. m. f.	Mechanical Stirring Time of stir.	Mechanical Stirring Read after stir.	Germanium Electrode, Oxygen Stirring E. m. f.	Oxygen Stirring Time of stir.	Oxygen Stirring Read after stir.	Germanium Electrode, Air Stirring E. m. f.	Air Stirring Time of stir.	Air Stirring Read after stir.
Ml.		*Volt*	*Volt*	*Min.*	*Min.*		*Min.*	*Min.*		*Min.*	*Min.*
0.0	1.98	0.3629	0.285	30	20	0.164	10	10	0.246	15	19
2.0	2.27	0.3803	0.293	7	18	0.181	5	7	0.262	6	18
4.0	2.75	0.4081	0.304	7	12	0.198	5	9	0.279	5	7
6.0	3.69	0.4636	0.327	7	15	...	..	..	0.306	5	10
8.0	4.39	0.5053	0.353	7	27	0.295	8	6	0.329	5	12
10.0	5.64	0.5782	0.401	7	12	0.346	4	10	0.380	5	13
12.0	6.70	0.6412	0.462	..	22	0.404	3	10	0.440	6	18
14.0	7.40	0.6826	0.512	7	12	0.455	4	13	0.492	5	12
16.0	8.56	0.7509	0.594	6	19	0.528	3	6	0.572	6	14
18.0	9.26	0.7927	0.645	8	14	0.575	3	7	0.628	5	9
20.0	10.17	0.8461	0.695	7	12	0.629	4	16	0.685	5	22
22.0	11.14	0.9070	0.735	6	12	0.683	4	8	0.714	6	24
24.0	11.55	0.9277	0.742	7	11	0.692	5	8	0.726	6	19
26.0	11.78	0.9412	0.749	8	20	0.704	3	4	0.740	6	14
28.0	11.94	0.9503	...	..	..	...	..	..	...	..	..

Fifty milliliters of a Prideaux-Ward universal buffer solution (*3*) were placed in a small beaker and an excess of insoluble germanium dioxide was added. The stick electrode was placed in the solution, the saturated calomel electrode was connected by means of a saturated potassium chloride bridge, and an intermediate vessel filled with a saturated solution of potassium chloride. The solution with the electrodes in contact was stirred mechanically and the initial reading taken during the stirring; the stirring was stopped and a second reading taken. This procedure was repeated at intervals throughout each observation.

Three experiments of this type showed that the electrode did not come to equilibrium in the course of a day, but that with constant stirring during the last 20 minutes of the observation, the value did not change greatly, thus giving the appearance that a constant value had been reached. Duplicate values could not be secured and the values obtained while the solution was being stirred were lower than those when the solution was not stirred.

This observed drifting of the electromotive force might be due to the solution in which the readings were made, a characteristic of the electrode itself which could be corrected only by proper pretreatment, or the particular gas which is present in the solution being measured.

In order to ascertain if the drifting was due to the type of solution used, experiments similar to the above were made using a 0.05 *M* potassium hydrogen phthalate solution and McIlvaine's buffer solution of pH 2.2. The readings were made both with no stirring and no insoluble germanium dioxide in the solution and with the insoluble germanium dioxide present and intermittent stirring. In all these experiments no reproducible constant value was obtained and any apparent equilibrium established was always destroyed by allowing the electrode to stand for a longer period thereafter. Apparently neither the presence nor absence of the insoluble germanium dioxide, nor the character of the solution in which the measurements are made is entirely responsible for the drifting shown by the electromotive force.

Attention was next directed to different methods of treating the surface of the electrode. It was hoped that such treatment might, as found with the antimony electrode, clean the electrode or coat it with a stabilizing film so that it would rapidly assume a reproducible equilibrium value in the solution. Treatment with nitric acid (1 to 1), plating with germanium, and treatment with hydrogen peroxide (perhydrol) were tried.

For the treatment with nitric acid, the electrode was immersed in a solution of nitric acid (1 to 1) for varying intervals of time. After each treatment with the acid, it was washed thoroughly with distilled water and then immersed in distilled water until it was used. This method of treatment did not yield an electrode which reached a constant reproducible electromotive force within a reasonable length of time. The values obtained varied about 40 millivolts over a period of one hour and were always higher when there was no insoluble dioxide present.

The effect of plating the electrode with germanium from a solution of germanium sulfate was next investigated. Measurements made with this electrode, in a manner similar to that used with the nitric acid–treated electrode, also showed large variations in the electromotive force over periods of 1 to 4 hours.

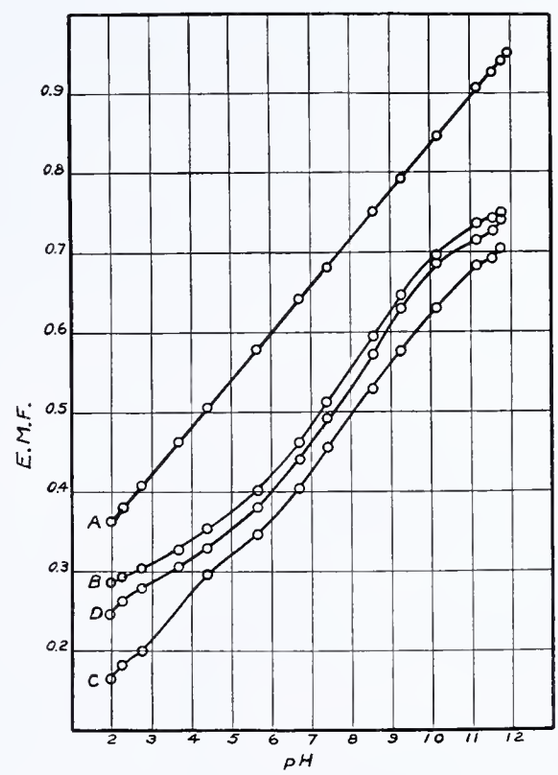

FIGURE 1

To investigate the effect of treatment with hydrogen peroxide, an electrode was immersed for 5 to 10 minutes in hydrogen peroxide, washed with distilled water, and then placed in the Prideaux-Ward universal buffer solution in which the measurements were made. When the electrode was not employed it was kept either in distilled water or in 3 per cent hydrogen peroxide. From a total of thirty-four experiments performed with a hydrogen peroxide–treated electrode it was found that at first there was a great change in the electromotive force but within an hour the value became fairly constant. However, this value is not reproducible and it will change if the electrode is removed and retreated or washed with distilled water.

The effect of stirring the solution with different gases was next investigated. Some McIlvaine buffer solution of pH 2.2 containing insoluble germanium dioxide was placed in a rubber-stoppered 150-ml. cylinder. The rubber stopper contained four holes, one was for the insertion of the germanium electrode and a second for the salt bridge connecting the calomel electrode with the solution. The gas was bubbled through a tube inserted in the third hole and reaching to the bottom of the solution. The excess gas found exit through a stopcock placed in the fourth hole, and opened only when gas was being passed through the solution. Readings of the electromotive force were taken while the solution was being stirred and after the stirring was stopped. Similar experiments were performed using purified air, nitrogen, hydrogen, and oxygen. Stirring with nitrogen appeared to give a fairly constant value of 0.273 volt on the first day at the end of about 2 hours, but on the second day it gave a value of 0.293 volt after 100 minutes. Hydrogen also failed to give a reproducible value. Air gave an initial value of 0.252 volt which changed to 0.272 volt over a period of 0.75 hour. Oxygen gave an initial value of 0.235 volt which varied between this value and 0.237 volt over a period of 1 hour. Of these four gases, nitrogen and hydrogen gave widely varying results, air gave more constant values, and the values with oxygen were fairly constant throughout the observation.

Although it was impossible to secure constant and reproducible electromotive force measurements with the germanium–germanium dioxide electrode in any of the buffer solutions used, it was deemed advisable to determine the relationship between pH and the electromotive force of this electrode. To obtain a variable pH, the Prideaux-Ward universal buffer solution was used and titrated with 0.2 N sodium hydroxide solution.

The relationship between the volume of sodium hydroxide used and the pH of the buffer solution was determined by measurements with a Bunker type of hydrogen electrode. The titration vessel, salt bridge, and saturated calomel electrode were all immersed in a thermostat, kept at 25° ± 0.05° C. Three titrations were made and the average results and the calculated pH values are given in Table I and Figure 1, curve A.

The titration of the Prideaux-Ward buffer solution was repeated with the germanium–germanium dioxide electrode in combination with a saturated calomel electrode.

Fifty milliliters of the buffer solution were placed in the titration cell, an excess of germanium dioxide was added, and the electrode inserted. Three different titrations were made, stirring the solution mechanically (curve B) and with oxygen (curve C) and air (curve D), both of the gases being first passed through potassium hydroxide solution and water. The solutions were first stirred and after the stirring was stopped the electromotive force was measured at intervals until it did not show much change in value. Following this some sodium hydroxide was added, the solution stirred for several minutes, and the intermittent reading repeated until an apparent constant value was obtained. This general procedure was used in all the titrations. The same apparatus was used for the gas stirring as in the previous experiments, except that there was one additional hole in the stopper for the buret. The results of these titrations with the time of stirring and the time after stirring when the apparent constant value was obtained, are also given in Table I and Figure 1.

From the preceding titrations it appears that the germanium–germanium dioxide electrode shows a potential difference against the saturated calomel electrode which is somewhat dependent upon the pH value of the solution. Mechanical stirring or stirring with purified air or oxygen did not give a straight-line relationship for the titration of the Prideaux-Ward buffer solution, although the titration performed by stirring with oxygen approached it fairly closely. In this latter case the variation approaches the relationship $E = 0.022 + 0.059$ pH between a pH of 3 and 11.

Equilibrium between the germanium electrode and the solution in which it is immersed cannot be obtained by long standing, stirring with purified air, nitrogen, hydrogen, or oxygen, or by special treatment of the electrode surface. This characteristic of the electrode is shown by the fact that it is impossible to obtain reproducible measurements in different samples of the same solution whether they are made on the same day or different days. In the study of the antimony electrode the presence of the trioxide made it possible to determine pH (*7*) from the electromotive force readings, but the presence of the insoluble germanium dioxide along with the metal electrode does not have a similar effect. If a stabilizing film does exist, it is different from any which has been employed here.

It is apparent that the electrode cannot, in its present condition, be used for accurate determinations of pH values but it may be of value in potentiometric titrations in which only the equivalence point of the reaction is sought. The results of the investigation of this use of the germanium–germanium dioxide electrode will appear in a subsequent paper.

Summary

A new germanium–germanium dioxide electrode, described above, shows a potential difference against a calomel electrode which is somewhat dependent upon the pH of the solution. The electrode was tested for pH determinations and found to be unsatisfactory. Treatment of the electrode surface with nitric acid (1 to 1), or hydrogen peroxide, or plating it with germanium failed to stabilize it. Stirring with purified oxygen, nitrogen, hydrogen, or air failed to stop the drifting of the electromotive force.

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Microchemical Methods in Toxicology

A. O. Gettler, of New York University and Bellevue Medical College, discussed the subject of "Microchemical Methods in Toxicology" at the Symposium on Recent Advances in Microanalysis, held April 26, 1935, at the New York Meeting of the American Chemical Society, and gave interesting accounts of many of his experiences in medico-legal work as toxicologist to the City of New York. He also described his work in proving that a small quantity of ethyl alcohol is normally present in the human brain, in which research he employed microtechnic extensively.

Potentiometric Titrations with the Germanium–Germanium Dioxide Electrode

M. L. NICHOLS AND S. R. COOPER, Department of Chemistry, Cornell University, Ithaca, N. Y.

IT HAS BEEN shown in a previous paper (*4*) that the germanium–germanium dioxide electrode shows a potential difference against a saturated calomel electrode which is somewhat dependent upon the pH value of the solution. The electromotive force values obtained with the present electrode were not sufficiently constant nor reproducible to allow it to be used for accurate pH determinations but it might be satisfactory for potentiometric titrations where only the equivalence point was desired. Therefore, an investigation was made to determine its applicability for the titration of acids, bases, and salts.

Experimental

Titrations of 0.2 *N* hydrochloric acid with 0.2 *N* sodium hydroxide were made by the same procedure as given in the previous paper (*4*) using both mechanical stirring (curve B) and stirring with air (curve C), freed from carbon dioxide. A check titration was made also using a Bunker-type hydrogen electrode (curve A). The curves plotted from the data of these titrations are given in Figure 1. These experiments show that the germanium–germanium dioxide electrode gives a titration curve similar to that given by the hydrogen electrode. In addition the equivalence points of the germanium and the hydrogen-electrode titrations, obtained by calculation of the maximum slope of the curves, agree within 0.1 ml. This indicates that the germanium electrode will give the equivalence point of an acid-base titration accurately. The solution may be stirred mechanically but more conveniently by using air, freed from carbon dioxide.

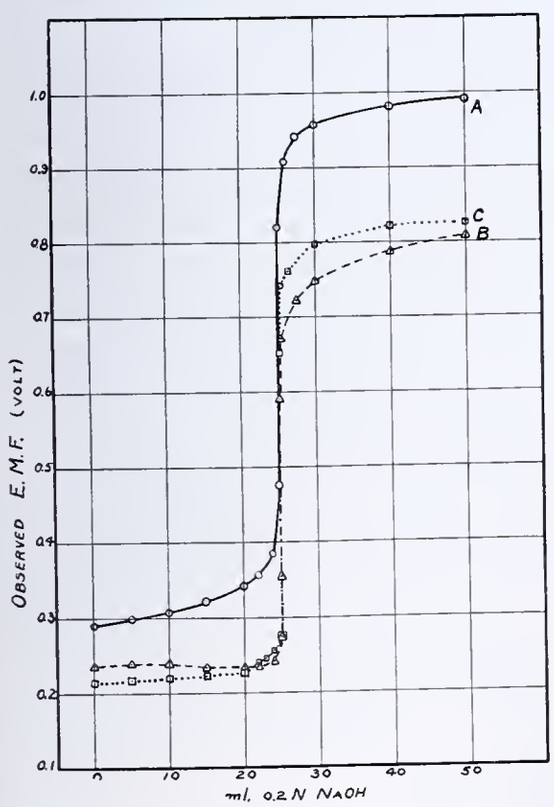

FIGURE 1

As the previous titrations were too time-consuming, they were repeated by a more rapid procedure both in the presence (curve A) and absence (curve B) of the insoluble germanium dioxide. The curves plotted from the data of these two titrations are given in Figure 2. In these titrations the time required for the titration was shortened from 5 to 6 hours to 2.25 hours without affecting the accuracy of the titration. Also the insoluble germanium dioxide did not have to be present in order to obtain the correct equivalence point for the titration.

Titrations of 0.1 *N*, 0.05 *N*, and 0.01 *N* solutions of hydrochloric acid and sodium hydroxide offered no difficulties. The end points of all the germanium electrode titrations agreed exactly with the titrations using the hydrogen electrode. As the strength of the solutions decreased, the sluggishness of the germanium electrode tended to make the end point less pronounced, but it was located easily for all of the strengths employed.

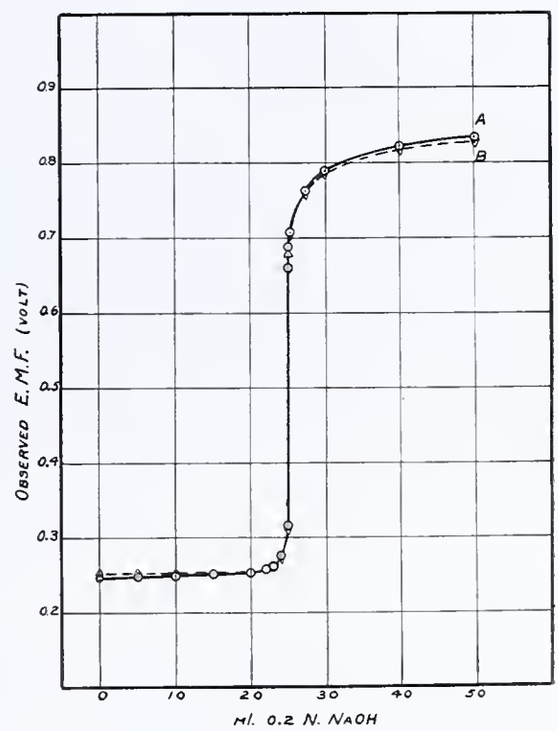

FIGURE 2

Having secured satisfactory results in the above titration without germanium dioxide, the same procedure, except that the time of stirring was shortened from 3 to 2 minutes, was used in all subsequent titrations. In this manner titrations were performed of monobasic acids, dibasic acids, weak bases, and salts. None of the solutions used in this part of the investigation were accurately standardized, but all of the titrations were checked with either a hydrogen or a quinhydrone electrode.

A summary of the titrations performed and the precision obtained is given in Table I. All the values given are the result of at least two check titrations with each electrode. The equivalent point volume was determined in each case by computing the maximum slope of the curve from the data obtained.

In addition to the above titrations, titrations of ammonium hydroxide with hydrochloric acid and the reverse

TABLE I. SUMMARY OF TITRATIONS

Solution Titrated	Approx. Normality	Titrating Solution	Approx. Normality	Equivalent Point Obtained	Checking Electrode	Diff. from Checking Electrode
				Ml.		*Ml.*
HNO_3	0.1	NaOH	0.1	23.1	Quinhydrone	−0.05
$HC_2H_3O_2$	0.1	NaOH	0.1	23.5	Hydrogen	0.0
$HClO_4$	0.1	NaOH	0.1	27.7	Quinhydrone	0.0
$C_6H_5CO_2H$	0.02	NaOH	0.02	23.55	Quinhydrone	−0.1
Lactic acid	0.1	NaOH	0.1	25.1	Hydrogen	0.0
CH_2ClCO_2H	0.1	NaOH	0.1	23.6	Hydrogen	0.0
HCO_2H	0.1	NaOH	0.1	23.2	Hydrogen	0.0
H_2SO_4	0.1	NaOH	0.1	23.5	Hydrogen	0.0
$H_2C_2O_4$	0.1	NaOH	0.1	23.3	Hydrogen	0.0
Tartaric acid	0.1	NaOH	0.1	26.0	Hydrogen	0.0
Malonic acid	0.1	NaOH	0.1	13.0	Hydrogen	0.0
				23.7		0.0
Succinic acid	0.1	NaOH	0.1	24.5	Hydrogen	0.0
o-Phthalic acid	0.05	NaOH	0.05	12.0	Hydrogen	0.0
				24.1		0.0
Salicylic acid	0.01	NaOH	0.01	22.6	Hydrogen	0.0
Maleic acid	0.1	NaOH	0.1	11.9	Quinhydrone	−0.1
				23.4		0.0
Fumaric acid	0.1	NaOH	0.1	23.5	Quinhydrone	−0.1
H_2CrO_4	0.05	NaOH	0.05	11.6	Hydrogen	−0.1
				23.7		+0.1
H_2CrO_4	0.05	NaOH	0.05	11.6	Air	0.0
				23.7		+0.2
NaOH	0.05	H_2CrO_4	0.05	26.0	....	...
H_3PO_4	0.1	NaOH	0.1	11.3	Hydrogen	0.0
				22.5		0.0
H_3BO_3	0.1	NaOH	0.1	24.0	Hydrogen	+0.1
Citric acid	0.1	NaOH	0.1	25.4	Hydrogen	0.0
HCl	0.05	Aniline	0.05	24.1	Hydrogen	0.0
Na_2CO_3	0.05	HCl	0.1	5.5	Hydrogen	0.0
				11.7		

with solutions ranging from 0.1 *N* to 0.01 *N*, titrations of 0.1 *N* and 0.05 *N* solutions of ethylamine with hydrochloric acid and the reverse, titrations of 0.05 *N* solutions of telluric acid with sodium hydroxide, titrations of 0.1 *N* solutions of sodium trinitride and sodium sulfite, and the back-titration of a solution of sodium sulfide were attempted, but in none of these cases could satisfactory results be obtained.

In a previous investigation (*4*) it was shown that although the germanium–germanium dioxide electrode shows a potential difference against a calomel electrode which is somewhat dependent upon the pH of the solution, constant and reproducible values could not be obtained. Titrations with this electrode make this characteristic more evident, for when several titrations were performed successively the initial electromotive force for each succeeding one was always higher than the former.

The electrode, without any insoluble dioxide in the solution to be measured, functions well as a hydrogen-electrode substitute in potentiometric titrations when the solution is stirred with purified air. Characteristic curves were obtained for monobasic acids, dibasic acids, tribasic acids, a weak base, and sodium carbonate. The results obtained in these cases are comparable to those which have been reported for the antimony electrode. In addition the electrode is satisfactory for certain titrations in which the hydrogen electrode is useless; its use in solutions of perchloric and nitric acids are examples of its action in solutions of strong oxidizing agents. No plausible explanation can be offered for the fact that in some cases the slope of the germanium electrode titration curve on the alkaline side is very much greater than that for a similar hydrogen electrode curve. Kolthoff and Hartong (*3*) obtained abnormal values of the electromotive force in titrations of tartaric acid with the antimony electrode, which they attributed to the formation of antimonyl tartrate, while Barnes and Simon (*1*) reported that this electrode did not function well in large quantities of hydroxy acids. Neither reason seems to offer a satisfactory explanation of the present case, and the difficulty may be due to the solubility of the germanium dioxide in sodium hydroxide.

The deportment of the germanium electrode in chromic acid solutions when the acid was titrated with a base was similar to that shown by the air electrode in that the electrode was first positive to a saturated calomel electrode, passed through zero, and was finally negative at the end. This is probably due to the high oxidizing potential of chromic acid. The antimony electrode showed a similar action in permanganate solutions (*3*), which was explained upon the assumption that the trioxide present was oxidized to the pentoxide. The germanium electrode gave lower electromotive force values in solutions in which the insoluble dioxide was present, but the difference was not of the magnitude of that displayed between chromic acid and other comparable acids. Doubtless some of the dioxide was formed in the chromic acid solution, but this does not explain the abnormal readings obtained. As no higher oxides of germanium are known, it is impossible to explain this action upon the basis of their formation.

Titrations of salts with this electrode gave poor results generally. Among those which were chosen, sodium carbonate alone was satisfactory, although difficulty was experienced in titrating it with both the hydrogen and germanium electrodes. The antimony electrode has been used for back-titrations of salts of hydronitric and sulfurous (*2*) acids, while the germanium electrode was found to be unsuitable.

The results obtained by using this electrode for titrations are very good, although at present no means has been perfected for stabilizing it so that it will give reproducible values satisfactory for determining absolute hydrogen-ion concentrations. The electrode, when once prepared, is rugged enough to last indefinitely; a mounted one has been in almost daily use for about a year. Then too, the ease with which nongas electrodes can be operated offers a great advantage of this electrode over the hydrogen electrode. Although most of the titrations which have been performed with the germanium electrode have consumed over 2 hours, it is possible that more rapid titrations can also be performed.

Summary

The germanium–germanium dioxide electrode, without the addition of the insoluble dioxide, functions well in potentiometric titrations of acids, bases, and salts. It has been used for the titration of hydrochloric, acetic, benzoic, lactic, monochloroacetic, formic, sulfuric, oxalic, tartaric, malonic, succinic, phthalic, salicylic, phosphoric, boric, and lactic acids with sodium hydroxide. Titrations of weak bases and salts with this electrode were unsatisfactory except in the case of

aniline and sodium carbonate. It has also been used in solutions of nitric, perchloric, maleic, and fumaric acids where the hydrogen electrode does not work satisfactorily.

The electrode was positive to a saturated calomel electrode in a 0.05 N solution of chromic acid, and as the acid was titrated with sodium hydroxide it passed through zero and finally became negative.

The germanium titration curves generally show a greater slope on the alkaline side than on the acid side.

The results of the titrations compare favorably with those obtained with the antimony electrode. The data for a titration curve of a monobasic acid can be obtained in 2.25 hours.

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Constant-Flow Orifice Meters of Low Capacity

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MANY devices, differing widely in principle of operation and in design, are employed for measuring the rate of flow of gases. The advantages and limitations of each device are well defined. The usual laboratory methods possess features which render them unsuitable for the metering of small amounts of gases, particularly when a constant rate of flow is required. The displacement type of meter, using the receiver method of measuring gas (typified by the "dry" meter used in the commercial metering of illuminating gas, the more accurate "wet" meter, and the spirometer) does not give an instantaneous reading of the rate of flow, but requires the measurement of the time interval during which a definite volume is passed. Anemometers and float meters are not only delicate but also inaccurate at low rates of flow. The method of measuring change in temperature of the gas due to the addition to it of a known quantity of heat has the disadvantage of not giving a direct reading of the rate of flow without complicated apparatus. Pitot tubes and venturi meters, while excellent in principle because of the comparatively small resistance they introduce into the line, are difficult and expensive to make, and unsuitable for measuring gases at rates of the order of 50 liters per minute or less.

The resistance-tube meters developed by Muster (*12*), and described by Guye and Schneider (*9*), were extensively used by the Chemical Warfare Service. In these meters the loss of head due to passing the gas through a capillary tube is a function of the rate of flow. Benton (*2*) gives detailed specifications for the calculation of dimensions and the construction of meters ranging from 500 cc. to 200 liters per minute in capacity. These meters are difficult to duplicate accurately and each one must be calibrated separately. They are fragile and not ideal for field use, but are unexcelled for metering pure gases at rates lower than 4 liters per minute. When the gas is contaminated with particulate matter, an appreciable error may be caused by the deposition of dust at the mouth of the capillary tube. Frequent cleaning becomes necessary and often proves difficult.

The orifice compares favorably with the resistance-tube meter. Orifices can be constructed in noncorrosive materials, are easily cleaned, and are satisfactory at fairly low rates of flow. At low pressure differentials, the rate of flow of gas through an orifice is a function of both the pressure above and the pressure below the orifice. This is also true in the case of the resistance-tube meter and the venturi meter. Both pressures must remain constant, or the rate of change of one must be a definite function of the rate of change of the other, to obtain a constant rate of flow. This result is very difficult to obtain without complicated and expensive compensating apparatus.

Constant-Flow Orifices

The problem of securing small constant rates of flow of gas has been solved practicably in this laboratory by the use of small orifices operating at pressure differentials greater than the critical, the pressure above the orifice being equal to or less than atmospheric pressure, and the downstream pressure being less than 0.53 times the upstream pressure. When an orifice is operated at a pressure differential equal to or greater than this definite critical value, the pressure below the orifice has no effect on the rate of flow (*11*); and for constant upstream pressures, a constant flow can be obtained through the orifice irrespective of wide variations in the downstream pressure. When a suction pump or ejector is used to create a less than critical pressure below the orifice, the only factors affecting the constancy of flow will be the atmospheric pressure and the resistance in the line above the orifice. In practically all cases these will remain constant within the allowable limits of error of the problem, but for accurate work a resistance compensator can easily be located above the orifice to insure constant rates of flow.

A constant-flow orifice was developed in this laboratory (*10*) which passed approximately 28.3 liters per minute (1 cubic foot per minute) of air when it was placed in the suction line below a modified Greenburg-Smith impinger, a dust-sampling instrument. The satisfactory performance of this and similar orifices which have been put to a wide variety of uses leads the author to believe that a description of this useful laboratory tool will be of interest.

Orifice Characteristics

The rate of flow of a gas through an orifice is a function of both the pressure above the orifice, P_1, and the pressure in the vena contracta, P. For an orifice with a smoothly rounded approach, P is the pressure in the throat. Coefficients for use with the theoretical discharge formulas for certain types of orifice operating under certain definite conditions have been determined accurately enough to allow the calculation of the rate of gas flow with high precision, without experimental calibration of each orifice. This holds for large orifices, which, if properly designed and installed with properly located pressure taps, serve as primary measuring instruments for low pressure differentials. The value of the coefficient decreases as the size of the orifice decreases, since the effects of skin friction and any irregularities due to construction vary inversely as the hydraulic radius. Unless very small orifices are made with extreme precision, the coefficient for each orifice should be calculated from an experimental calibration if the orifice is to be used for precise measurements.

If a gas flows adiabatically through an orifice, and if it is assumed to act as a perfect gas under the condition of entrance to the orifice, the weight of gas discharged through the orifice (*8*) is given by the following formula:

$$M = A\sqrt{\frac{2g\gamma}{\gamma - 1} \cdot \frac{P_1}{V_1}\left[\left(\frac{P}{P_1}\right)^{2/\gamma} - \left(\frac{P}{P_1}\right)^{(\gamma+1)/\gamma}\right]} \qquad (1)$$

where M = grams of gas per second
A = area of throat of orifice in sq. cm.
g = gravity constant
γ = ratio of specific heats of the gas = Cp/Cv
P_1 = absolute pressure on the entrance side of the orifice in grams per sq. cm.
P = absolute pressure in the throat of the orifice
P_2 = absolute pressure below the orifice
V_1 = specific volume of the gas on the entrance side of the orifice in cc. per gram
T_1 = absolute temperature of the gas on the entrance side of the orifice in degrees Centigrade

The general gas law for a perfect gas is expressed by the formula:

$$PV = BT \text{ or } P/V = P^2/BT \qquad (2)$$

If the gas being measured is air, then $B = 2930$, and $\gamma = 1.4$, so that by letting $g = 981.5$ cm. per sq. second and substituting in Formula 1 one obtains the equation:

$$M = 1.531\,\frac{P_1A}{\sqrt{T_1}}\left[\left(\frac{P}{P_1}\right)^{10/7} - \left(\frac{P}{P_1}\right)^{12/7}\right]^{1/2} \qquad (3a)$$

or

$$M = 1.531\,\frac{P_1A}{\sqrt{T_1}}\,(K) \qquad (3b)$$

From Formula 3 it is evident that the weight of air discharged depends upon the two pressures, P_1 and P, and varies directly as K. The maximum discharge will occur when K reaches its maximum value—i. e., when $P/P_1 = 0.53$. This also is the minimum possible value for P and is called the

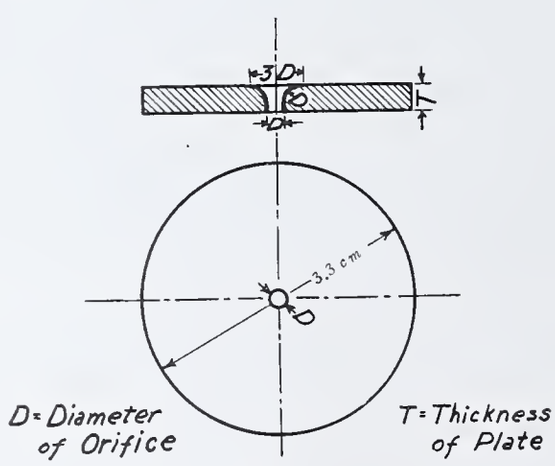

Figure 1. Sketch of Orifice

critical pressure Pm. It is an orifice characteristic that if $P_2 \geq Pm$, then $P = P_2$, but if $P_2 < Pm$, then $P = Pm$ (*11*). Consequently, for any value of P_2 equal to or less than 0.53 P_1, the weight of gas discharged will depend only on P_1. This was shown to be true by Napier in 1866 when he proved experimentally that the weight of steam discharged from an orifice was independent of the pressure of the medium into which efflux took place at pressure differentials greater than the critical (*6*).

This phenomenon was explained by Zeuner (*14*) on the hypothesis that "the air flows (through an orifice) into a vacuum with the acoustic velocity corresponding to the state of the air in the orifice, no matter what resistance exists during the flow toward the orifice." The velocity of efflux is constant as long as T_1 is constant and is independent of P_1, although the quantity of gas delivered depends upon this pressure owing to its effect on the density. If the velocity of the gas passing through the orifice is calculated, using Formula 3 as the basis for calculations, one finds that the velocity of air becomes equal to the velocity of sound, in air at the same pressure and temperature, when $P_2 = 0.53\ P_1$ approximately. This is the maximum discharge velocity, equal to the velocity of discharge into a vacuum, and beyond this point P_2 ceases to exert a back pressure on the air coming through the orifice. Substituting 0.53 for P/P_1 in 3a one obtains the formula:

$$M = 0.812\ P_1A/\sqrt{T_1} \qquad (4)$$

which is the same as Fliegner's formula (*7*) (expressed in c. g. s. units) when P_2 is less than the critical pressure.

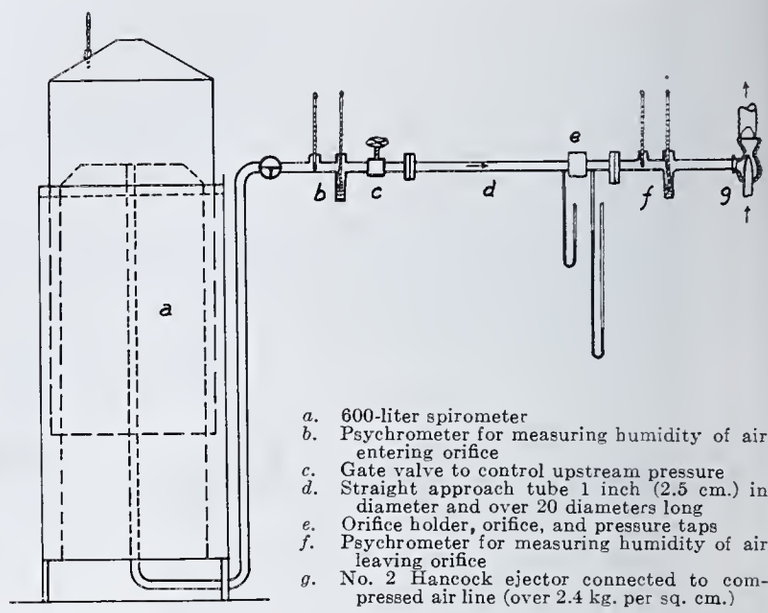

Figure 2. Apparatus for Calibrating Orifice Flowmeters

Design and Construction of Orifices

Careful consideration was given to the form of orifice to be used. There are very few data in the literature on the characteristics of small orifices of any type operating at the critical pressure differential. Circular orifices with curved approach were adopted, since they were considered to be the easiest type to duplicate, they have a relatively high coefficient, and this coefficient is only slightly altered by wearing of the orifice edge. Figure 1 is a sketch of the type of orifice tested. Eighteen orifices, made with standard twist (tap) drills varying from No. 40 to No. 60, were calibrated.

In making an orifice, a brass blank of the required thickness was soldered to the end of a 2.5-cm. brass rod centered in the lathe, and the blank was turned down to 3.3 cm. diameter. The orifice was then drilled in the blank with a standard tap drill held in the lathe foot-stock. The rounded approach was cut by hand with a three-cornered scraper and the curvature was checked with a template. The rod was then removed from the lathe and heated until the orifice plate dropped off, the solder being wiped off while hot. All burrs and rough places were removed from the lower rim of the orifice until it would pass a microscopic inspection.

This method did not allow accurate duplication of orifices, but can be followed easily by an amateur mechanic. It

allows a rough prediction of the area of the finished orifice, but the true area must be accurately measured with a microscope. Orifice numbers denote the drill used in making them, but measured areas were used in all calculations of coefficients. Table I lists areas, diameters, and thicknesses of orifices.

TABLE I. DIMENSIONS OF ORIFICES

Orifice No.	Theoretical Area for Tap Drill Used	Measured Area (A)	Diameter Orifice ($D = \sqrt{4A/\pi}$)	Thickness of Plate (T)
	Sq. cm.	*Sq. cm.*	*Cm.*	*Cm.*
40	0.04865	0.05171	0.2568	0.310
40a	0.04865	0.04997	0.2522	0.277
42	0.04381	0.04672	0.2438	0.310
44	0.03748	0.03949	0.2243	0.310
46a	0.03323	0.03581	0.2136	0.239
46	0.03325	0.03488	0.2108	0.310
48b	0.02929	0.03125	0.1994	0.246
48a	0.02929	0.03039	0.1966	0.312
48	0.02929	0.03029	0.1963	0.310
50a	0.02484	0.02541	0.1798	0.310
50	0.02484	0.02530	0.1796	0.310
52	0.02013	0.02136	0.1649	0.310
52a	0.02013	0.02029	0.1608	0.239
54a	0.01536	0.01616	0.1435	0.310
54	0.01536	0.01562	0.1410	0.320
56	0.01071	0.01143	0.1207	0.320
60	0.00813	0.01014	0.1135	0.310
58	0.00897	0.00928	0.1037	0.310

Calibration of Orifices

The apparatus used in calibrating the orifice flowmeter is shown in Figure 2. All joints were sealed and tested for tightness.

The spirometer had been previously calibrated by a water-displacement method. The air-filled spirometer was connected to a sealed tank filled with water, which had a valved outlet opening into a weighing tank. As water was drawn from the tank, an equal volume of air was drawn from the spirometer. The air in the spirometer was completely saturated with water vapor and temperatures were kept constant. The volume of the spirometer between the 500- and the 300-liter marks, and between the 300- and 100-liter marks, was calculated from these data.

In conducting the tests, most of the runs were made for the volume of air contained between the 500- and the 100-liter marks on the spirometer, although a few runs were made between the 500- and 300-liter marks. Air was drawn through the orifice from the room until the upstream pressure had been regulated and then the source of air supply was switched to the spirometer. The stopwatch used in timing was started as the 500-liter mark passed the indicator and was stopped when the 100-liter mark passed. The following data were secured for each point on the calibration curve:

Wet- and dry-bulb temperatures of the room
Barometric pressure and temperature
Dry-bulb temperature of spirometer air
Wet- and dry-bulb temperature of air above orifice
Wet- and dry-bulb temperature of air below orifice
Pressure above orifice
Pressure below orifice
Time for measured volume of air to pass orifice

All these factors were kept as constant as possible during any one run. The upstream pressure was varied from atmospheric pressure to atmospheric minus 30 cm. of water, and from atmospheric minus 2.5 cm. of mercury to atmospheric minus 25.4 cm. of mercury.

Theoretical discharge quantities were computed at 21.11° C. (70° F.) (T_1 = 294.2° A) and at the absolute test pressure, P_1, expressed in terms of centimeters of mercury. By substituting in Formula 4 letting 1 gram/sq. cm. = 0.0736 cm. of mercury—i. e., $P_1' = P_1/0.0736$—one obtains the working formula: where P_1' = the pressure in cm. of mercury.

$$M = 11.03\ P_1'A \qquad (5)$$

The measured volume of air discharged was converted to equivalent volumes at 1 atmosphere (76.0 cm. of mercury) and 21.11° C. This corrected volume divided by the time gave the flow in liters per minute. These values are plotted against the pressure, P_1, in Figure 3. The volumes per minute were corrected for moisture content and converted to actual discharge, M', in grams per second. Wet-bulb thermometer readings taken in the upstream supply line were corrected for error in depression due to the velocity of the air. Corrections were calculated from charts given by Carrier and Lindsay (*5*), and were very small in all cases. After the air passed the psychrometer, the vapor content could not increase; and, since the pressure was falling while the temperature remained nearly constant, the vapor in the expanding mixture was becoming more dilute and farther from saturation, so that there was no tendency for water to be precipitated. The composition of the moist air remained unchanged along the line and was the same at the orifice as at the psychrometer in the supply pipe. This could be checked by the readings from the psychrometer below the orifice (*3*). The partial pressure of water vapor in the air was calculated from the corrected psychrometer readings by means of Carrier's psychrometric chart (*4*). In calculating the theoretical discharge, the upstream pressure, P_1, was calculated on the basis of a mercury column at 21.11° C. In the tests the temperature of the column was never over 8° C. warmer than this and the error in manometer readings introduced by this temperature variation was negligible.

The actual discharge, M', when divided by the theoretical discharge, M, as given by Fliegner's Formula 5 gave the coefficient of discharge, C:

$$M' = CM \qquad (6)$$

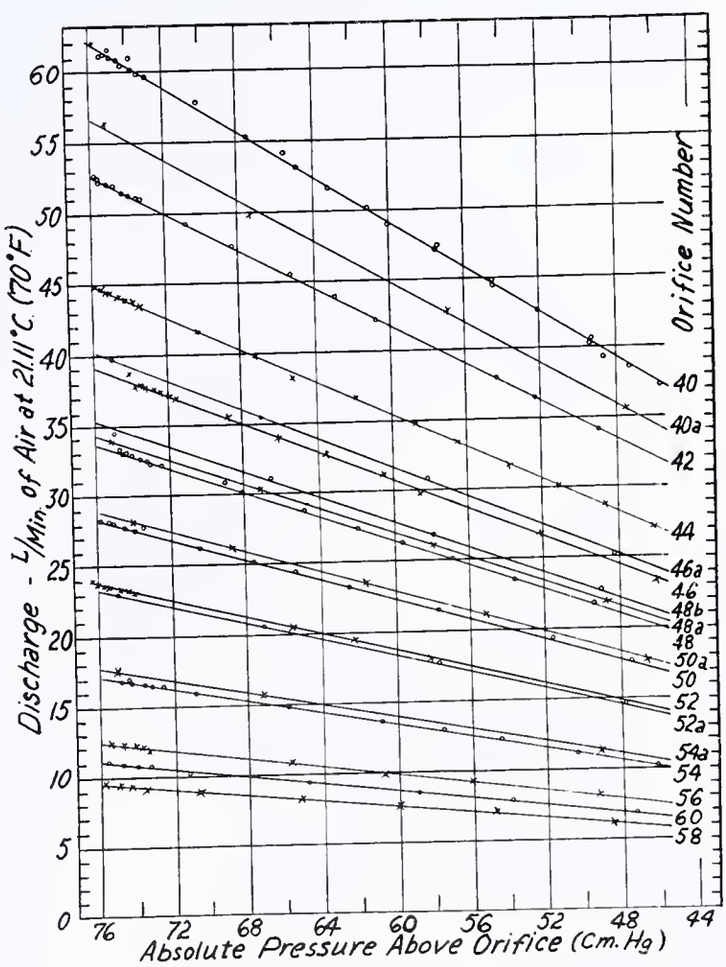

FIGURE 3. DISCHARGE OF AIR THROUGH ORIFICES AT 21.11° C. AND 85 PER CENT RELATIVE HUMIDITY

The values of the coefficient of discharge as determined in this investigation include the factors of velocity of approach, viscosity, irregularities of construction, and differences between actual and assumed conditions. Because of the effect of the last two factors and the limited number of observations on each orifice, there is a large probable error in any equation for the discharge coefficient formulated from these

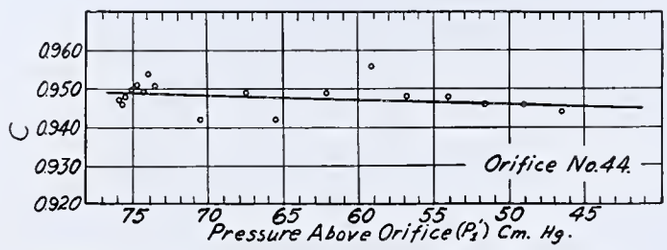

FIGURE 4. VALUES OF COEFFICIENT OF DISCHARGE

For use with Fliegner's formula for stated pressures above orifice 44.

data. The data show a trend in the value of the coefficient which appears to indicate that it is a direct function of both orifice area and upstream pressure. This may be only an apparent effect with irregularity of construction acting as the controlling factor, but similar results have been reported by other experimenters. Polson, Lowther, and Wilson (*13*) determined coefficients for orifices of 0.6 to 2.5 cm. diameters when air under pressure discharged into the atmosphere with pressure drops in the critical range, and found that values of C for use with Fliegner's formula varied directly with area and upstream pressure. Similar results with respect to area were reported by Bean et al. for impact nozzles of similar shape (*1*).

Each value of C was plotted against P_1 for each orifice. Equations for the straight line of best fit were determined by means of the method of least squares. A typical curve for one orifice is shown in Figure 4. The values of C were calculated from these equations for each orifice at pressures of 50.8, 63.5, and 76.2 cm. of mercury, and these values of C were plotted against area of orifice A. Orifice 58 was dropped from the calculations at this point, since it was markedly irregular in form. The equations of the straight lines of best fit for the

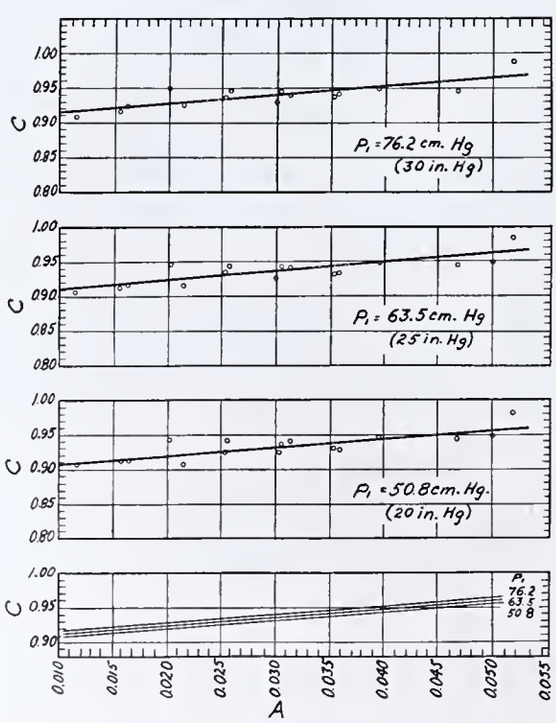

FIGURE 5. VARIATION OF COEFFICIENT WITH RESPECT TO AREA AT DIFFERENT PRESSURES ABOVE ORIFICE

variation in the value of C, with respect to the value of A when the value of P_1 is stated, were calculated by application of the method of least squares. These lines are shown graphically in Figure 5.

These orifices were made by two people using the same technic so far as possible. Individual differences were not evident. If the area of an approximately circular orifice is accurately measured, the value of C is given approximately by the following equations. If the flow must be measured with a high degree of accuracy, each individual orifice should be calibrated for at least three points on the curve, and the value of C can then be calculated.

Equations for C

The following equations for C were calculated from the experimental data with respect to orifice area (cm.^{2}) at the given upstream pressures:

P_1 Cm. Hg	P_1 (Inches Hg)	Equation for C
50.8	(20)	$C = 0.897 - 48.12A$
63.5	(25)	$C = 0.899 - 50.83A$
76.2	(30)	$C = 0.904 - 49.15A$

The probable error of the above equations was ±0.6 per cent—values of C as determined from the straight line of best fit from the C versus P_1 graph for any one orifice were as likely to deviate less than ±0.6 per cent from the values obtained by solving the above equations as they were likely to deviate more than ±0.6 per cent. Individual observations for the relation between C and P_1 on any individual orifice showed a probable error of approximately ±1.0 per cent. The assumption of straight-line relationship is allowable within the range in pressures and orifice areas investigated.

Comments and Conclusions

The object of this investigation was twofold: first, to develop a set of constant flow orifices for laboratory use, and second, to study the characteristics of these orifices. In accord with laboratory practice, results have been expressed in metric units.

The author's showed that small circular orifices to give constant flows of gas under critical pressure differentials could be easily made for laboratory use; that the rate of flow for any given upstream pressure could be calculated with a probable error of approximately ±1.0 per cent for an orifice of measured throat area, but that for more accurate determination of rates of flow, the orifice should be calibrated against a satisfactory primary standard.

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Reflux Regulator for Laboratory Stills

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IT IS A well-known fact that the reflux ratio—moles of vapor returned to the column as refluxed liquid per minute divided by moles of vapor collected as distillate per minute—is one of the most important factors governing fractional distillations of mixtures consisting of compounds with similar boiling points. A number of reflux regulators have been described in the literature (*1–15*) in recent years, and while each of these may possess a certain advantageous feature, it was felt that there was considerable room for improvement upon the present methods used for measuring and controlling the reflux ratio of laboratory stills.

The most important requirements for an ideal reflux regulator may be set forth as follows:

1. The refluxed liquid should be at its boiling point when it is being returned to the column. If this is not the case, additional condensation of an unknown amount of vapor will take place in the column with the obvious result that the actual reflux ratio would be larger than that measured by the reflux regulator.
2. The "hold-up" of the reflux regulator should be small in relation to the "hold-up" of the column.
3. In order to avoid contaminating the distillates with dissolved stopcock lubricant all stopcocks should be eliminated, particularly from lines through which liquid or hot vapors pass.
4. The reflux ratio should be easily adjustable during the course of a distillation. Normally an infinite reflux ratio is desired until equilibrium in the column has been established, whereafter the reflux ratio is maintained at a finite value which may vary within wide limits (2:1 to 100:1) during the distillation, depending upon the difficulty encountered in the particular stage of the fractionation.
5. The exact value of the reflux ratio should be easily determinable at any time during a distillation. In other words, it is not sufficient to have a regulator set at 10 to 1 and then simply vary this value to less than 10 to 1, more than 10 to 1, etc.
6. When distilling mixtures of unknown composition it is desirable to be able to maintain a definite value of the reflux ratio without necessitating any calculations and extrapolations based upon the heats of evaporation, molecular weights, composition, densities at the boiling point, etc.
7. The reflux regulator, when once calibrated with one liquid, should be ready for use at any time for any other liquid or mixture of liquids without further calibration.
8. The reflux ratio should be independent of the rate of distillation, or, in other words, the regulator when once set at a definite value should maintain this reflux ratio even if the rate of boiling in the still pot should change within wide limits.
9. The regulator should return the reflux to the column at a uniform rate rather than operate intermittently on the siphon principle.

With the above requirements as an ultimate goal, a number of different types of reflux regulators were developed in this laboratory. By combining the best features of each of these a reflux regulator was finally developed which fulfills all the original requirements and has been found satisfactory for laboratory stills.

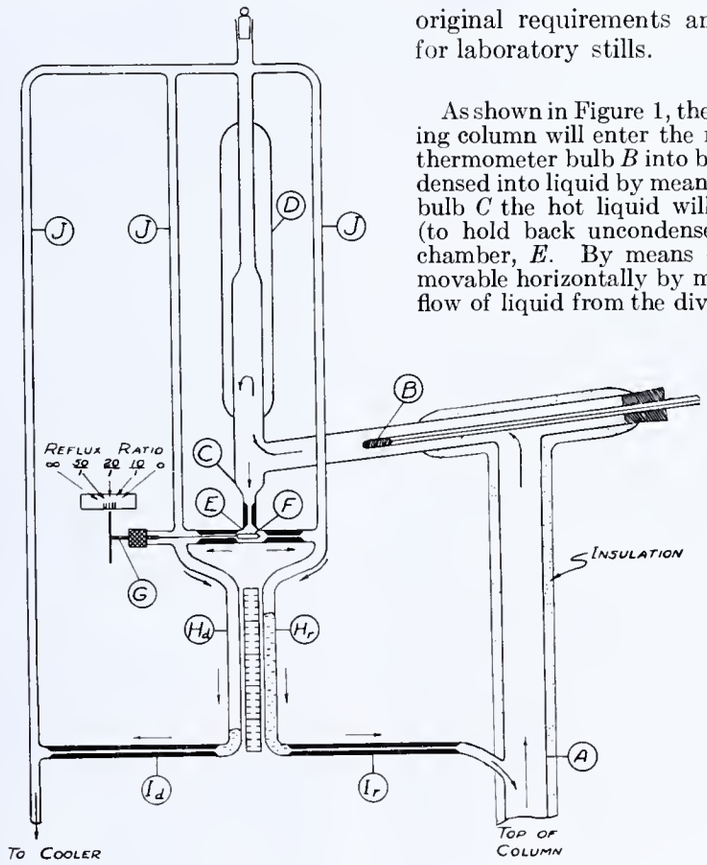

Figure 1. Reflux Regulator

As shown in Figure 1, the vapors from the top of the rectifying column will enter the reflux regulator at *A* and pass over thermometer bulb *B* into bulb *C*, where the vapors will be condensed into liquid by means of the reflux condenser, *D*. From bulb *C* the hot liquid will pass through a vertical capillary (to hold back uncondensed vapor) into the small dividing chamber, *E*. By means of a cylindrical metal plunger, *F*, movable horizontally by means of a micrometric screw, *G*, the flow of liquid from the dividing chamber, *E*, may be carefully controlled. Thus, a certain amount (90 per cent, for example) of the liquid may be returned to the still as reflux by allowing it to pass through the vertical tube, H_r, and through the horizontal capillary, I_r, back into the top of column *A*. The remaining part of the liquid (10 per cent) may be taken over as distillate by passing it through the vertical tube, H_d, and through the horizontal capillary, I_d, into a cooler (not shown in the figure).

Inasmuch as the capillary tubes, I_d and I_r, are identical in size and length, it is evident that the amount of liquid flowing through them will be directly proportional to the hydrostatic heads in the vertical tubes, H_d and H_r, respectively, the numerical values of which may be read by means of the vertical millimeter scale.

The numerical value of the reflux ratio employed at any time during a distillation is obtained by dividing the scale reading on the right, H_r, by that on the left, H_d.

An increase or decrease in the reflux ratio may be obtained simply by turning the micrometric control screw, *G*, to the left or right, respectively. When *G* and *F* are at the extreme left, no distillate whatsoever is obtained; hence this setting corresponds to an infinite reflux ratio. As indicated by the horizontal scale above the micrometer screw, it is possible to obtain approximately any desired reflux ratio by means

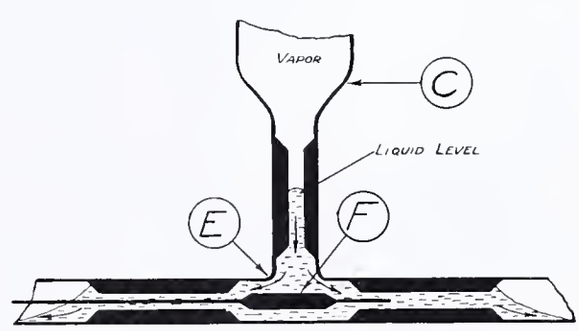

Figure 2. Detail of the Dividing Chamber

of a single micrometer setting. The exact adjustment of the desired reflux ratio is obtained by a subsequent setting of the micrometer screw based upon the scale readings of H_r and H_d.

Pressure equality in the vapor space on both sides of the capillary tubes is insured by the equalizing lines, *J*. For

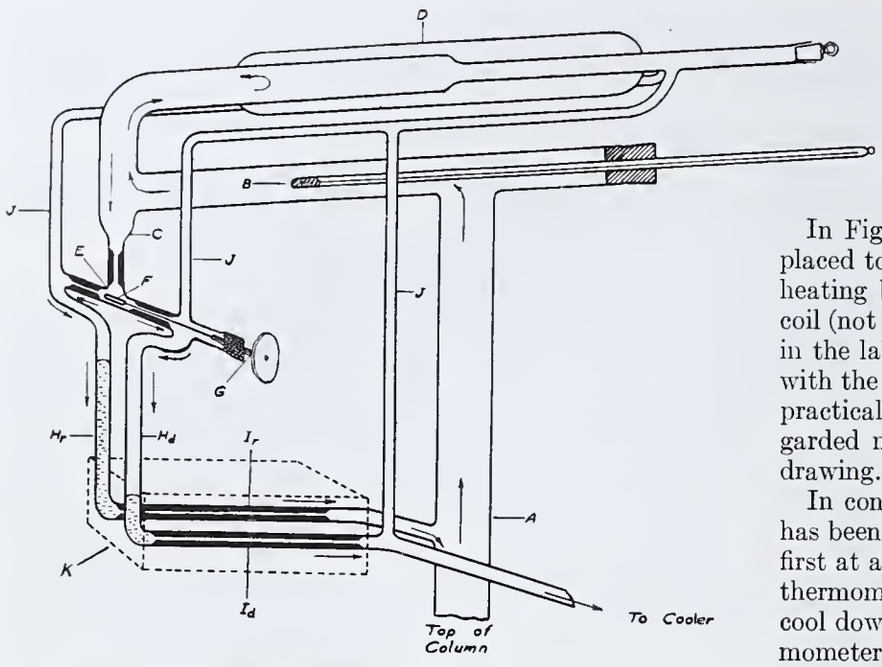

FIGURE 3. REFLUX REGULATOR WITH TEMPERATURE CONTROLLED CAPILLARIES

mixtures boiling near room temperature it may be desirable to provide these equalizing lines with small condensers.

Figure 2 is a detail sketch of the dividing chamber with the metal plunger. From this it is evident that by moving the metal plunger toward the left the flow of liquid will be diverted toward the right, and vice versa. It should be noted that since the reflux ratio is determined by means of the scale readings of H_d and H_r (Figure 1), irregularities in the dimensions of the cylindrical metal plunger or of the dividing chamber do not affect the accuracy of the reflux regulator.

During its passage through the reflux regulator it was found that the liquid in the two capillary tubes, I_d and I_r, would cool down several degrees below its boiling point. In order to avoid this it is necessary to heat the liquid in I_r (by surrounding the capillary with a heating coil) prior to its reëntry into the column.

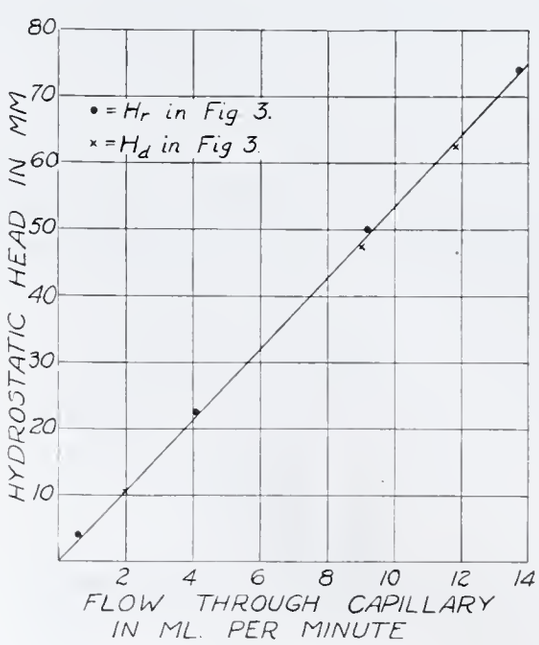

FIGURE 4. CALIBRATION CURVE

For accurate work it is also important that the temperatures of the liquid in the two capillaries, I_d and I_r, be identical, since the viscosity and, therefore, also the flow, as well as the hydrostatic heads in H_d and H_r, and consequently $\frac{H_r}{H_d}$, or the reflux ratio, are functions of the temperature of the liquid. For this reason the reflux regulator in Figure 1 has been modified as shown in Figure 3 (this regulator is made by the Otto R. Greiner Company, 55 Plane Street, Newark, N. J.).

In Figure 3 the two horizontal capillary tubes have been placed together, so that they may be installed inside a small heating box, K, provided with a thermometer and heating coil (not shown in figure). In order to conserve vertical space in the laboratory the condenser has been placed at an angle with the column. This reflux regulator is more compact and practical than the one shown in Figure 1, which should be regarded more as an explanatory diagram than as an actual drawing.

In contrast to the conventional method, the thermometer has been placed in a position so that the vapors will strike it first at a point above the bulb. By striking the stem of the thermometer the superheated vapors will have a tendency to cool down to the true boiling point before reaching the thermometer bulb. It should also be noted that the amount of vapor passing the thermometer bulb when the reflux ratio is 20 to 1, for example, is 21 times the actual rate of distillation. Because of this fact an unusual constancy is obtained in the thermometer readings, even during distillations at a very low rate.

The important dimensions of Figure 3 are, naturally, those of the capillary tubes, I_d and I_r. If these tubes are made of 0.9 mm. capillary tubing 100 mm. long, a hydrostatic head of 60 mm. will correspond to a rate of about 12 ml. per minute for a liquid such as benzene. For greater rates of flow the capillary tubes may be made correspondingly shorter than 100 mm., or the height of H_d and H_r may be increased above 60 mm. For flows of benzene up to 50 ml. per minute, capillary tubes of 1.0-mm. bore 50 mm. long will produce a hydrostatic head of about 60 mm. It is important that the two capillaries be of identical size and that they be sealed perfectly horizontally.

Figure 4 is a calibration curve of a reflux regulator of the type shown in Figure 3, with capillaries of 0.9 × 100 mm. As shown by this figure, the flow of liquid (benzene at its boiling temperature) is directly proportional to the hydrostatic head.

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RECEIVED June 18, 1935.

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CORRESPONDENCE

The Spectrophotometric Determination of Manganese in Steel

SIR: In a recent article [IND. ENG. CHEM., Anal. Ed., 7, 27 (1935)] J. P. Mehlig suggested the use of the spectrophotometer for the colorimetric determination of manganese. He proposed to eliminate entirely the use of permanent standards in this way. Nineteen standard solutions of permanganate were measured at four different wave lengths to furnish empirical calibration curves relating transmission to concentration. It is the object of this brief note to show that if the simple, fundamental optical principles of colorimetry had been employed in this case, very little calibration would be necessary.

For a system which obeys the Lambert-Beer law we may write:

$$I = I_0 \, 10^{-ecd} \qquad (1)$$

where I_0 is the incident light intensity
I is the emergent light intensity
c is the concentration in moles per liter
d is the thickness of the solution layer in cm.
e is the molecular extinction coefficient

or

$$\log \frac{I_0}{I} = ecd = E \qquad (2)$$

where E is the extinction.

Some spectrophotometers have a portion of the scale calibrated directly in E. In any case the transmittancy $\frac{I}{I_0}$ can be read directly and, if e is known, c can be calculated. Mehlig's nineteen values for $\lambda = 520$ mμ yield a value of

$$e = 2.24 \times 10^3$$

A single precise measurement of a standard permanganate solution, protected against fading by a small amount of periodate, was made on a Bausch and Lomb spectrophotometer and gave the value:

$$e = 2.23 \times 10^3$$

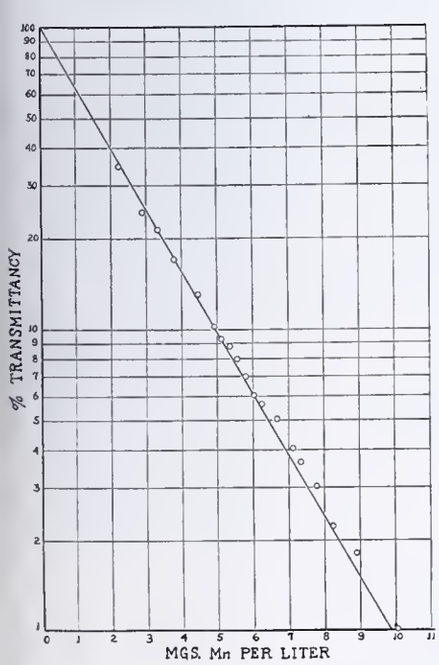

FIGURE 1

The agreement is well within the average deviation of the e values calculated from Mehlig's data. Figure 1 shows a straight line passing through the origin and having a slope computed from our value of $e = 2.23 \times 10^3$. The circles indicate Mehlig's observations. (The abscissas are expressed in milligrams per liter instead of moles per liter in order to conform to the original data.) Figure 1 illustrates several important points.

1. Beer's law is obeyed over the concentration range employed.
2. Deviations from the straight line are plainly revealed, which is not the case in a smooth empirical curve.
3. The average slope of the straight line is more reliable than any individual calibration point.
4. A few accurate determinations yielding a straight line provide a reliable value for e and no reference to a curve is necessary. All subsequent measurements can be computed by means of Equation 2.

An added advantage which is obvious from Equation 2 is the possibility of computing the results for any thickness d. The empirical calibration method would require a different curve for every thickness. The results which are reported on manganese determinations in steel show excellent agreement with other methods. It is felt, however, that the procedure is needlessly laborious, in that separations are not absolutely necessary in the photometric method.

Conclusion

A few precise measurements of transmittancy over the concentration range will reveal the reliability of a spectrophotometric method, if the results are computed or plotted in accordance with the Lambert-Beer law. For many substances the extinction coefficients may be found in the literature, in which case, if they are sufficiently reliable and exact for the purpose, no calibration of the spectrophotometer is necessary. It is understood, of course, that the instrument must be calibrated in the physical sense. This is especially true with respect to the wave-length calibration [Gibson, K. S., *J. Optical Soc. Am.*, 21, 564–87 (1931)].

The author's statement that "the spectrophotometric method has no advantage over the volumetric bismuthate method" and that "they are to be regarded as alternate procedures" is unfortunate. The spectrophotometer is a costly but very precise instrument if it is used properly. If its employment invariably involved laborious empirical calibration as described, this would undoubtedly be a strong deterrent to its wide use. Such is rarely the case.

RALPH H. MÜLLER

WASHINGTON SQUARE COLLEGE
NEW YORK UNIVERSITY
NEW YORK, N. Y.
May 17, 1935

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SIR: In the work recently reported under the title "Spectrophotometric Determination of Manganese in Steel," the writer was especially interested in the establishment of a reference curve correlating transmittancy at a given wave length with manganese concentration and preferred to use such a curve rather than the method suggested by R. H. Müller in his recent note. If the most careful work is done, the amount of data required for constructing the curve is little more than is necessary for calculating the average slope of a straight line. Once constructed, the curve is just as easy to use in determinations as is a straight line and it is even simpler to read off from the curve the manganese concentration for a given transmittancy than to solve the equation log $T = ecd$ for c in a given determination.

It was already evident from the results obtained by the writer that Beer's law is obeyed over the concentration range employed:

In constructing the straight line in his Figure 1 Müller should have used an average value for e instead of a value calculated from a single measurement supposed to be precise, since an analyst can never be certain that a single observation is precise. How many atomic weight values have been based upon a single determination?

The empirical calibration method does not require a different curve for every thickness d, since the transmittancy for the desired cell length may be calculated from data secured with another length by means of the fundamental Lambert's law equation

$$T_1 = T_2^{\frac{d_1}{d_2}}$$

where T_1 and T_2 are the respective transmittancies for thicknesses d_1 and d_2. This calculation is very easily made by means of the special K. and E. slide rule.

The writer felt that it would be safer as a general policy to separate the manganese in his procedure, since such separation makes the method universally applicable without question. As yet it has not been proved that the separation of manganese is not absolutely necessary in either spectrophotometric or photoelectric methods which are to have general application.

So far as the determination of manganese in steel is concerned, the spectrophotometric method has no advantage over the volumetric bismuthate method, because the latter gives just as good results without the necessity of separating the manganese and rarely requires any dilution. The spectrophotometric method, however, does have a decided advantage over colorimetric methods which require a series of standards.

The strongest deterrent to the wide use of the spectrophotometer is the cost of the instrument rather than any so-called laborious, empirical calibration that may be involved. It is naturally understood that the instrument, if used at all, is used properly.

J. P. Mehlig

Oregon State College
Corvallis, Oregon
June 28, 1935

Note to Authors

In the preparation of manuscripts authors should address themselves to specialists in their particular fields, rather than to the general reader. If the article describes a new method, the author should endeavor to tell the complete story, so that the reader will not have to wait for succeeding contributions or duplicate the unpublished tests in order to find out whether he can apply the method in his own work.

The following is suggested as a general outline to be followed in preparing analytical methods for this edition:

1. Preliminary statement or introduction, in which the need for the method should be stated, brief reference to other methods or literature given, etc.
2. Experimental:
   - Outline of proposed method
   - Description of apparatus and reagents
   - Procedure
   - Data:
     - Interfering substances or conditions
     - Concentration range through which the method is applicable
     - Accuracy of the method
     - Precision of the method
3. Discussion and summary

The author should state at the outset why he thinks the paper is worth publishing. If it deals with a method of analysis, he should give some comparison with established methods in point of speed, applicability, accuracy, and cost. Extensive reviews of the literature should not be given and such references as are cited should be carefully checked. Incorrect references are inexcusable and cast doubts on the author's reliability. The theoretical considerations on which the method is based should be clearly set forth.

In the experimental part, previously published or well-known procedures which have been followed should only be designated or references given to them. If, however, the method is new, the data upon which it is based should be presented but in no greater detail than is necessary to prove its soundness. New procedures should be clearly described, that readers can easily duplicate the work. Loose directions should be avoided, unless the author knows that no possible harm can result from the most liberal interpretation that can be made of such expressions as "to the faintly acid solution," "wash the precipitate," "ignite," etc. If new or uncommon reagents are needed, the author should state their probable cost, where they can be purchased if rare, or how they can be prepared, if not on the market.

The author should distinguish carefully between precision and accuracy. Briefly but somewhat roughly stated, accuracy is a measure of degree of correctness; precision is a measure of reproducibility. The precision of a result does not necessarily have anything to do with its accuracy; it serves merely as a measure of the duplicability of the procedure in the hands of a given operator. No claim for accuracy should be made unless the author believes that he has satisfactorily established the correct result.

The author should be frank and define the limitations of the method. Tests dealing with the effects of foreign compounds should be made on mixtures in which the ratios of the compounds sought to the foreign compounds are varied and simulate conditions that are likely to be encountered in practice. If the author has made no such tests, he should state that he has no knowledge of the effects of foreign substances. It is desirable that possible applications of methods should be stated.

A summary or prefatory abstract should acquaint the reader with the main points of the article. This should give concisely where possible the substances determined, nature of material to which determination is applicable, interfering substances, range of concentration to which method is applicable, whether or not a sensible constant error is involved—that is, the accuracy of the method—and its precision. Either the summary or the prefatory abstract is so often used by abstractors that the author may well spend considerable time in their preparation, in order to be certain that proper emphasis is given to the main features of the contribution.

Our "Suggestions to Authors" is available to those unfamiliar with the form of manuscript and illustrations preferred by Industrial and Engineering Chemistry.

ANALYTICAL EDITION

INDUSTRIAL AND ENGINEERING CHEMISTRY

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NOVEMBER 15, 1935

HARRISON E. HOWE, EDITOR

Direct Simultaneous Microdetermination of Carbon, Hydrogen, and Oxygen

II. Analysis of Pure Compounds Containing Carbon, Hydrogen, Oxygen, and Sulfur

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THE purpose of this paper is (1) to extend the development of the direct simultaneous microdetermination of carbon, hydrogen, and oxygen to compounds which also contain sulfur; (2) to get information regarding the ultimate fate of the sulfur present in different types of linkage in organic compounds, after being subjected to combustion; and (3) to study the mechanism of the reaction between oxides of sulfur and the absorbents which are present in the combustion tube filling.

The elementary analysis of organic substances containing sulfur has caused relatively little difficulty. Different investigators seem to disagree as to whether sulfur dioxide or trioxide is the final oxidation product of the sulfur present in the molecule. It is common practice to remove either, or both, of these substances by the addition of a suitable absorbent to the combustion tube filling. The absorbents generally used are lead chromate or lead peroxide, both of which fix the oxides of sulfur as relatively nonvolatile lead sulfate. The efficacy of metallic silver as an absorbent for oxides of sulfur was pointed out by Dennstedt (*1*), but its use for this purpose seems to have been completely overlooked.

In the direct determination of oxygen by an oxidation process it is important to know whether sulfur dioxide or trioxide is formed. If both are formed, the proportion of the one to the other must be determined, since more oxygen is consumed in forming sulfur trioxide than in forming the dioxide. In most previous investigations using this method, it has been assumed that either sulfur dioxide (*2*) or sulfur trioxide (*3, 15–18*) is the sole final oxidation product of the sulfur present in the molecule.

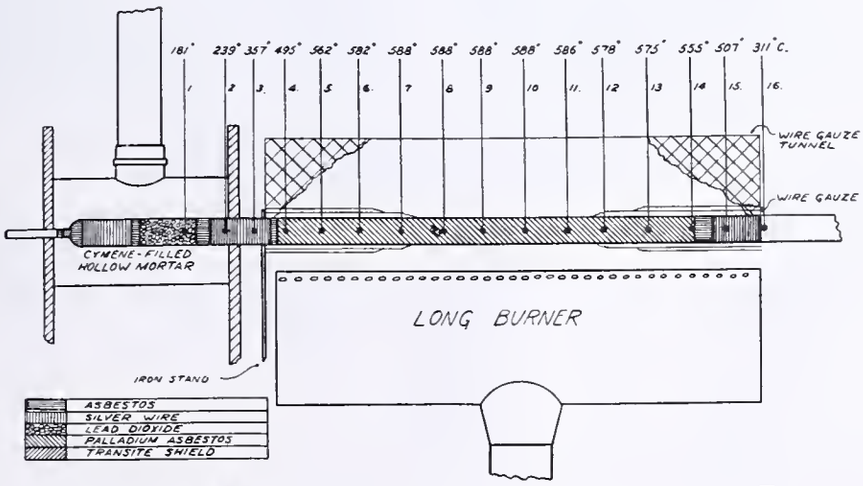

FIGURE 1. TEMPERATURES EXISTING IN MICROCOMBUSTION TUBE

In the direct determination of oxygen by other methods the presence of sulfur has caused complications (*14*). In their hydrogenation method, ter Meulen and Heslinga (*13*) found it necessary to make slight modifications in their procedure when sulfur was present in the compound being analyzed. All the hydrogen sulfide was held on the nickel catalyst in the combustion tube only if the temperature was not too high. The ordinary procedure was therefore modified by heating the end of the combustion tube, which contained the nickel-asbestos catalyst, to a temperature of only 150° C. and then no hydrogen sulfide escaped. The catalyst was rapidly poisoned by the sulfur but sufficed for one analysis. An important improvement to ter Meulen's method for analyzing sulfur-containing substances has recently been reported by Marks (*12*). In his work a thoria-promoted nickel catalyst was used which was found to be quite resistant to poisoning by sulfur. Anhydrous calcium sulfate was used for absorption of the water formed; this absorbent does not retain ammonia, hydrogen sulfide, or carbon dioxide.

Experimental

The apparatus and procedure used in the present investigation were identical to that already described (*9*).

In order to get information regarding the effect of the type of sulfur linkage present in the compound on the direct determination of oxygen, two substances were selected for analysis. The first was a sulfone, which would be expected to yield sulfur dioxide when subjected to thermal decomposition (*7*), and the second was a sulfonic ester, which would be expected to yield sulfur trioxide on thermal decomposition (*8*).

From theoretical considerations one would predict that the extent of the oxidation of the sulfur in the substance analyzed would be a function of the sulfur dioxide–sulfur trioxide equilibrium at the

temperature existing in the combustion tube. There was a large excess of oxygen always present and the temperature of the palladium asbestos catalyst varied from a maximum of 588° C. down to a minimum of about 425° C. before the gases reached absorbents which made further equilibration impossible. Figure 1 illustrates the combustion tube and its filling and shows the temperatures which existed at various points in the tube. These temperatures were measured with a chromel-alumel thermocouple imbedded in the palladium-asbestos with oxygen flowing at the rate of 3 cc. per minute. The conditions existing during these temperature measurements were made to simulate, as closely as possible, those of the actual determinations. The combustion tube had an internal diameter of 8 mm., so that with this gas flow the linear flow rate was 1 cm. in 12.8 seconds.

Under these conditions one would expect 99 to 100 per cent of sulfur trioxide as the final product, since, according to Knietsch (*10*), who made a study of the equilibrium reaction

$$2SO_3 \overset{Pt}{\rightleftharpoons} 2SO_2 + O_2$$

under conditions similar to those used here, the percentages of sulfur trioxide shown in Table I exist at the indicated temperatures.

Table I. Sulfur Dioxide–Trioxide Equilibrium

(According to Knietsch)

Temperature	SO_3
° *C.*	%
300	76[a]
350	95[a]
400	100
450	99
500	96
550	88
600	80

[a] Equilibrium not attained.

Table II gives the experimentally determined values for the "oxygen consumed" and also the calculated values, assuming in one case that sulfur trioxide and, in the other, that sulfur dioxide is the total final oxidation product of the sulfur.

Column 4 indicates that the found values are higher than the calculated values by a practically constant amount. The theoretical amount of sulfur present in the compounds was used in these calculations; in calculations made on unknown substances the percentage of sulfur present must be determined by an independent analysis. Column 5 gives the weight of oxygen equivalent to the weight of sulfur in the sample—i. e., the weight of oxygen involved in each single stepwise oxidation of the sulfur present. There is a close agreement between the figures in columns 1 and 6. The average value of the found oxygen consumed is 99.78 per cent of that calculated, assuming SO_4 formation. These figures are brought out in columns 7 and 8. The mean difference (column 7) corresponds to approximately the limits of accuracy of the gasometric determination of the oxygen consumed. However, since these differences all have the same sign and since the temperature (about 425° C., Figure 1) existing in the combustion tube at the point where the gases encounter the metallic silver after having passed over the catalyst is such that one would expect a small amount (1 per cent or less) of sulfur dioxide to still be present, it is also possible (*4*) that the discrepancy between the figures in columns 4 and 5 is due to the incomplete oxidation of the sulfur to sulfur trioxide and then to SO_4.

On the basis of these results it would appear that the lead peroxide in the combustion tube filling is not concerned in the absorption of the oxides of sulfur. If any oxides of sulfur reached the lead peroxide they would react according to Equations 1 and 2:

$$PbO_2 + SO_2 = PbSO_4 \quad (1)$$
$$2PbO_2 + 2SO_3 = 2PbSO_4 + O_2 \quad (2)$$

Experimentally, from the determined oxygen consumed, and theoretically, from the temperature which existed in the combustion tube, it is reasonably certain that sulfur trioxide is the predominating product of the oxidation of the sulfur present in the samples. If any sulfur trioxide came into contact with the lead peroxide an atom of oxygen would be evolved for every molecule of trioxide which reacted, whereas actually an additional atom of oxygen was consumed for every molecule of sulfur trioxide present.

While several investigators (*5, 6, 11, 19*) have demonstrated that lead peroxide is a quantitative absorbent for oxides of sulfur, it was Dennstedt (*1*) who showed that metallic silver is also capable of quantitatively absorbing sulfur trioxide, forming silver sulfate, the increase in weight being due to the addition of SO_4.

In order to demonstrate that the silver had absorbed the oxides of sulfur, the silver filling in the middle of the combustion tube and in the rear of the tube adjacent to the position occupied by the boat was removed and added to distilled water containing a few crystals of barium chloride. A white precipitate immediately formed which consisted of a mixture of silver chloride and barium sulfate, the former being due to the metathetical reaction between silver sulfate and barium chloride. After digesting on the steam bath for a short time the characteristic curdy precipitate of silver chloride could be recognized. After cooling, the mixture was made alkaline with a few drops of concentrated ammonium hydroxide solution. The curdy silver chloride precipitate dissolved, leaving a fine silky precipitate which, after digestion on the steam bath, formed the microcrystalline precipitate characteristic of barium sulfate. Work is being started in this laboratory using this reaction as the basis for a microacidimetric method for the determination of sulfur in organic compounds.

The absorption of the sulfur trioxide by the metallic silver therefore fully explains the results obtained in the present work. Either the sulfur burns directly to sulfuric acid, as postulated by Dennstedt (in the presence of excess oxygen and water formed during the combustion), and then reacts with the silver, or, as seems more likely, the sulfur trioxide reacts directly with the silver, forming silver sulfite, which then immediately oxidizes to sulfate. Whatever the mechanism, this reaction satisfactorily explains the amount of oxygen which is consumed during the combustion of a sulfur-containing substance. It is immaterial whether the sulfur is eliminated from the sample as dioxide or trioxide during thermal decomposition, the final yield of trioxide being the same.

Table II. Determination of Oxygen Consumed

Compound	Oxygen Consumed: Found	Calculated, based on formation of: SO_3	SO_2	Found minus calculated (SO_3)[a]	To convert SO_2 to SO_3 or SO_3 to SO_4	Calculated, based on formation of SO_4[b]	Difference	
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*[c]	%[d]
Diphenyl sulfone	16.204	15.705	15.181	0.499	0.524	16.229	−0.025	99.85
	16.348	15.876	15.347	0.472	0.529	16.405	−0.057	99.65
Phenyl *p*-toluene sulfonate	15.707	15.276	14.799	0.431	0.477	15.753	−0.046	99.70
	16.784	16.287	15.778	0.497	0.509	16.796	−0.012	99.93
						Mean	−0.035	99.78

[a] Column 1 − column 2.
[b] Column 2 + column 5.
[c] Column 1 − column 6.
[d] Column 1 ÷ column 6.

Table III. Illustrating Method of Calculation

	Mg.
Weight of sample (diphenyl sulfone)	7.137
Weight of carbon dioxide, found	17.283
Weight of water, found	2.982
	%
Carbon, found	66.05
Carbon, theory	66.01
Difference	+0.04
Hydrogen, found	4.68
Hydrogen, theory	4.62
Difference	+0.06
	Cc.
Volume of oxygen at start (738.88 mm., 298.42° K.)	87.698
Volume of oxygen at start, NTP	78.026
Volume of mercury added	12.102
Volume of oxygen at end (736.47 mm., 300.79° K.)	75.607
Volume of oxygen at end, NTP	66.521
Volume of oxygen at end, NTP plus correction (0.166 cc.)	66.687
Volume of oxygen consumed, NTP	11.339
	Mg.
Weight of SO_4 formed, theory	3.143
Weight of oxygen consumed, found	16.204
Weight of actual oxygen consumed (found ÷ 99.78)	16.240
Weight of oxygen consumed, theory (based on SO_4 formation)	16.228
Difference	+0.012
Weight of oxygen in carbon dioxide, found	12.569
Weight of oxygen in carbon dioxide, theory	12.564
Difference	+0.005
Weight of oxygen in water, found	2.648
Weight of oxygen in water, theory	2.617
Difference	+0.031
Weight of oxygen in SO_4	2.094
Sum of oxygen in combustion products, found	17.311
Sum of oxygen in combustion products, theory	17.275
Difference	+0.036
Oxygen in sample, found (O_2 in combustion products minus O_2 consumed)	1.071
Oxygen in sample, theory (O_2 in combustion products minus O_2 consumed)	1.047
Difference	+0.024
	%
Oxygen in sample, found	15.01
Oxygen in sample, theory	14.67
Difference	+0.34

Table IV. Results

Compound	Sample	Found C	Found H	Found O	Oxygen consumed	Difference from Theory C	Difference from Theory H	Difference from Theory O	Oxygen consumed	S
	Mg.	%	%	%	*Mg.*	%	%	%	*Mg.*	%
Diphenyl sulfone	7.137	66.05	4.68	15.01	16.204	+0.04	+0.06	+0.34	+0.012	14.70
	7.215	65.78	4.67	14.72	16.348	−0.23	+0.05	+0.05	−0.021	14.70
Phenyl *p*-toluenesulfonate	7.404	62.85	4.95	20.10	15.707	−0.01	+0.08	+0.76	−0.013	12.92
	7.894	62.90	4.98	19.97	16.784	+0.04	+0.11	+0.63	+0.025	12.92
					Mean	−0.04	+0.08	+0.45 ±0.12	+0.002 ±0.008	

Results

To illustrate the method of calculation, the complete data are given in Table III for one of the compounds. The actual oxygen consumed is obtained by dividing the found oxygen consumed by 99.78, the mean percentage difference between the found and theoretical oxygen consumed, based on SO_4 formation. This is justified by the possibility that a small amount of sulfur dioxide still persists in the combustion gases.

Finally, Table IV gives the summarized data for the two pure compounds analyzed.

The hydrogen determinations, particularly in case of the phenyl *p*-toluenesulfonate, are in error by amounts greater than desired. It is primarily this error which causes the error in the oxygen determination to reach the magnitudes indicated, since errors in the hydrogen determination are multiplied by 8 and errors in the carbon determination are multiplied by 2.67 in terms of oxygen. Although the samples were dried for some time in a vacuum desiccator over sulfuric acid, it may be that these substances tenaciously hold moisture.

Summary

The direct, simultaneous microdetermination of carbon, hydrogen, and oxygen has been extended to include compounds also containing sulfur.

Regardless of whether the sulfur linkage is such that, on thermal decomposition, sulfur dioxide or trioxide is primarily formed, the sulfur appears in the final combustion gases as sulfur trioxide, although it is possible that exceedingly small amounts of sulfur dioxide may also be present.

The sulfur trioxide is absorbed by the metallic silver present in the combustion tube filling and is quantitatively retained as silver sulfate, an atom of oxygen being consumed in converting the sulfur trioxide to SO_4.

Four analyses made on two different compounds indicate that the results are accurate to about 0.4 ± 0.1 per cent. The errors in the method are primarily due to the rather large multiplication of errors made in the determination of carbon and hydrogen. The gasometric determination of the oxygen consumed is of satisfactory accuracy.

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(Part III follows)

III. Analysis of Pure Compounds Containing Carbon, Hydrogen, Oxygen, and Nitrogen

THE purpose of this paper is to extend the development of the direct microdetermination of carbon, hydrogen, and oxygen in organic compounds to substances containing nitrogen, and to study the influence of the type of nitrogen linkage present upon the ultimate fate of the nitrogen after complete combustion of the sample.

The presence of nitrogen in organic compounds has always been a complicating factor in elementary analysis, necessitating the addition of some substance to the combustion tube filling which would either absorb any oxides of nitrogen formed by oxidation of the nitrogen present in the sample, or reduce them to elementary nitrogen. In the direct determination of oxygen by an oxidation process, the simultaneous presence of nitrogen introduces additional complications and, in many cases (*16, 17, 18*) has made the direct determination of oxygen impossible. In the gasometric combustion method (*4, 5*), it has previously been assumed that the nitrogen present in the samples analyzed was completely converted to elementary nitrogen, even in the case of trinitrobenzene (*5*). It is certainly difficult to visualize how the three nitro groups in trinitrobenzene could be completely deoxidized to elementary nitrogen in an atmosphere of oxygen.

In their hydrogenation method, ter Meulen and Heslinga (*11*) had to modify their procedure slightly when analyzing compounds containing nitrogen because the nitrogen appeared both as ammonia and in the elementary state. Analysis of an amide, oxime, nitro, and azo compound by a modification of this method (*14, 15*) generally yielded over 50 per cent of the nitrogen in the sample as ammonia, regardless of the type of nitrogen linkage present.

In the combustion of an organic nitrogen-containing compound, the nitrogen does not appear in the combustion products in any single combination unless the combustion tube filling contains a reagent which is capable of performing the necessary reaction (*2, 9, 12*). Any contrary assumption is not in agreement with the facts. Hence, in the direct determination of oxygen by an oxidation process it is important to know the amount of oxygen involved in the oxidation of the nitrogen present—i. e., the fate of the nitrogen after complete combustion of the sample.

Experimental

The apparatus and procedure used in the present work were identical to that already described (*7*). Five pure organic nitrogen-containing compounds were analyzed, the percentage of nitrogen varying from 5.6 to 10.4 per cent and the oxygen from 8.1 to 16.1 per cent. In order to get information regarding the effect of the type of nitrogen linkage on the ultimate fate of the nitrogen after complete combustion of the sample, the compounds selected had the following types of nitrogen linkages: (1) amido, (2) amino, (3) heterocyclic, (4) nitrile, and (5) nitro.

The "oxygen consumed" was first calculated, entirely neglecting the fact that nitrogen was present. The results are shown in Table I.

From Table I it is observed that, on the basis of oxygen consumed, the compounds group themselves into two classes: the found oxygen consumed is (1) less than the theoretical, and (2) greater than the theoretical. Strebinger (*17*) and also Staněk and Nemes (*16*) found, for the substances they studied, a similar division into two classes. One class, in which the nitrogen was quantitatively converted into ammonia and gave satisfactory results for oxygen consumed, likewise contained amino and amido groups. The other class, in which the oxygen consumed could not be successfully determined, because of the formation of a mixture of nitric acid and nitrogen, contained nitro, heterocyclic, azo, osazone, hydrazone, and betaine nitrogen.

Before proceeding to the determination of the oxygen content of the samples analyzed, using the combustion data obtained and including their nitrogen content, it was necessary to have some information as to the ultimate fate of the nitrogen present. It is assumed that, in the complete combustion of an organic substance, two distinct reactions occur: (1) the thermal decomposition of the substance, followed by (2) complete oxidation of the pyrolytic products. The rate of oxidation and the final state of equilibrium are determined by factors such as the amount of oxygen available, the temperature existing in the combustion tube, and the presence of catalysts and absorbents in the combustion tube filling. Sufficient oxygen should always be present so that this does not become a limiting factor and the rate of gas flow should be slow enough to permit complete equilibration under the conditions existing in the combustion tube before the gases reach any absorbent.

Table I. Theoretical and Observed Oxygen Consumed

Compound	N_2	Oxygen Consumed: Found	Oxygen Consumed: Theoretical (neglecting nitrogen)	Oxygen Consumed: Diff.	Oxygen Consumed: Found/Theory
	%	*Mg.*	*Mg.*	*Mg.*	%
Benzanilide	7.11	20.460	20.655	−0.195	99.06
p-Aminoacetophenone	10.37	16.593	16.785	−0.192	98.86
2-Phenylquinoline 4-carboxylic acid	5.62	18.252	17.855	+0.397	102.22
	5.62	18.307	17.932	+0.375	102.09
γ-Phenoxybutyronitrile	8.70	19.263	18.747	+0.516	102.75
	8.70	17.586	17.055	+0.531	103.11
p-Nitrobiphenyl	7.04	15.052	14.608	+0.444	103.04

If the thermal decomposition of the substances is first considered, it is noted that only the amino and amido groups have hydrogen attached to the nitrogen atom. It is postulated that these groups are split out of the molecule during the thermal decomposition, either directly as ammonia (recent evidence, *19*, as to the thermal decomposition of primary amines would indicate this to be the mechanism), or possibly as free amino or imino radicals which could then unite with hydrogen, formed during the same reaction, to form ammonia. The ammonia (or possibly the free amino or imino radicals) would then be subjected to oxidation and thermal dissociation under the conditions existing in the combustion tube. Since the nitrogen in these groups is attached to carbon as well as to hydrogen, other possible simple thermal scission products would include cyanogen and hydrogen cyanide. The compounds containing the nitrile and the heterocyclic nitrogen would, on this basis, be expected to yield cyanogen and possibly hydrogen cyanide. The nitro compound would be expected to yield nitrogen peroxide and cyanogen and possibly also nitric oxide and hydrogen cyanide. The complete list of simple thermal decomposition products expected would then include ammonia (or amino and imino free radicals), cyanogen, hydrogen cyanide, nitrogen peroxide, nitric oxide, and also elementary nitrogen, which might be evolved from nitrogen-containing cokes which are often formed during combustion.

Oxidation of the nitrogen-containing thermal decomposition products by the excess of oxygen present in the combustion tube at temperatures from the maximum of 600° C. (*8*) down to 181° C., the temperature of the lead peroxide, would

yield only nitrogen peroxide and nitrogen (*1, 6, 10, 13*). The proportion of these two substances which finally results, under a given set of conditions, should primarily be a function of the manner in which the nitrogen is linked in the molecule.

With the combustion tube filling used in the present work, the nitrogen peroxide was absorbed by lead peroxide. According to Dennstedt (*3*), this reaction yields only lead nitrate. However, in an investigation conducted on the above reaction in this laboratory, the details of which will be communicated later, it was found that the reaction was not as simple as indicated above. When nitrogen peroxide was passed through a weighed microabsorption tube containing lead peroxide at a temperature of about 185° C., the increase in weight corresponded best with

$$2NO_2 + 2PbO_2 = Pb(NO_3)_2 + PbO + {}^1/_2O_2$$

This equation agrees with the increase in weight of the lead peroxide absorption tube and also with the fact that lead nitrate is formed, which could be extracted from the mixture of lead oxide and peroxide, as was done by Dennstedt. According to the above equation, an atom of oxygen is liberated each time a pair of nitrogen peroxide molecules react with the lead peroxide and must be considered in the calculation of the oxygen consumed. The calculations given later were all based on the use of the following equation:

$$2C_xH_yO_zN + nO_2 + 2PbO_2 \longrightarrow 2xCO_2 + yH_2O + Pb(NO_3)_2 + PbO$$

n = number of molecules of oxygen necessary to balance the above equation

On the basis of the above hypothesis regarding the fate of the nitrogen in the samples, the calculation of the oxygen content of the substances was undertaken. The theoretical amount of nitrogen present was used in these calculations: In studying substances of unknown composition the percentage of nitrogen must be determined by an independent analysis. Taking the combustion data collected for the first sample analyzed (benzanilide) and by a method of trial, the proportion of nitrogen peroxide and nitrogen assumed to be formed was varied until the determined and theoretical values for oxygen consumed agreed. Agreement occurred when 26 per cent of the nitrogen was considered to be in the form of nitrogen peroxide and 74 per cent as nitrogen. Using these figures, together with the combustion data, gave satisfactory agreement between the determined and theoretical oxygen content of the substance.

Since the combustion characteristics of *p*-aminoacetophenone are similar to benzanilide, as shown in Table I, it was expected that application of the same nitrogen peroxide–nitrogen ratio to the calculations made on the former substance would lead to a similar satisfactory agreement between the found and theoretical oxygen consumed and oxygen content of this substance. This was found to be the case despite the fact that the percentage composition of the two substances was quite different.

The combustion characteristics of the second group of substances, as indicated in Table I, are different from the first group. It was therefore anticipated that the nitrogen peroxide–nitrogen ratio applied to the first group would be invalid if used in the calculations on the second group of substances. This was confirmed. According to the hypothesis advanced above, the ratio of nitrogen peroxide to nitrogen should be much greater in the second group than in the first group. Using the method of trial mentioned previously it was found that when the ratio of 59 per cent nitrogen peroxide to 41 per cent nitrogen was used in the calculations made on the first substance analyzed in this group, satisfactory agreement was obtained between the found and theoretical oxygen consumed and the oxygen content. Satisfactory agreement was also obtained between all of these values when the same ratio was applied in the calculation of the data obtained for the other members of the group despite rather wide variations in the percentage composition of the substances analyzed.

To illustrate the method of calculation, the complete data for one of the substances analyzed are given in Table II.

Table II. Illustrating Method of Calculation

	Mg.
Weight of sample (benzanilide)	8.342
Weight of carbon dioxide, found	24.197
Weight of water, found	4.179
	%
Carbon, found	79.11
Carbon, theory	79.15
Difference	−0.04
Hydrogen, found	5.61
Hydrogen, theory	5.63
Difference	−0.02
	Cc.
Volume of oxygen at start (743.66 mm., 297.66° K.)	87.700
Volume of oxygen at start, NTP	78.734
Volume of mercury added	15.945
Volume of oxygen at end (741.66 mm., 297.70° K.)	71.771
Volume of oxygen at end, NTP	64.251
Volume of oxygen at end, NTP plus correction (0.166 cc.)	64.417
Volume of nitrogen (assuming complete conversion to N_2)	0.474
74 per cent of this volume	0.351
Actual volume of oxygen at end = corrected end volume minus 74 per cent of nitrogen volume	64.066
Volume of actual oxygen consumed	14.668
	Mg.
Weight of actual oxygen consumed, found	20.961
Weight of oxygen necessary for complete combustion of carbon and hydrogen in sample, theory	20.655
Weight of nitrogen peroxide formed by complete combustion of nitrogen in the sample	1.947
Weight of oxygen in this nitrogen peroxide	1.354
26 per cent of this weight of oxygen	0.352
Weight of oxygen consumed, theory (including 26 per cent NO_2 formation)	21.007
Difference (theory minus found)	−0.046
Weight of oxygen in carbon dioxide, found	17.598
Weight of oxygen in carbon dioxide, theory	17.607
Difference	−0.009
Weight of oxygen in water, found	3.711
Weight of oxygen in water, theory	3.725
Difference	−0.014
Weight of oxygen in nitrogen peroxide (26 per cent formation)	0.352
Sum of oxygen in combustion products, found	21.661
Sum of oxygen in combustion products, theory	21.684
Difference	−0.023
Oxygen in sample, found (O_2 in combustion products minus O_2 consumed)	0.700
Oxygen in sample, theory (O_2 in combustion products minus O_2 consumed)	0.677
Difference	+0.023
	%
Oxygen in sample, found	8.39
Oxygen in sample, theory	8.12
Difference	+0.27

The complete data for all of the analyses are summarized in Table III.

Table III. Results

Compound	Weight of Sample	Found C	Found H	Found O	Actual oxygen consumed	Difference from Theory C	Difference from Theory H	Difference from Theory O	Oxygen consumed	N
	Mg.	%	%	%	*Mg.*	%	%	%	*Mg.*	%
Benzanilide	8.342	79.11	5.61	8.39	20.961	−0.04	−0.02	+0.27	−0.046	7.11
p-Aminoacetophenone	7.267	71.04	6.69	11.57	17.230	−0.03	−0.03	−0.27	−0.003	10.37
2-Phenylquinoline 4-carboxylic acid	7.830	77.06	4.36	11.95	18.457	−0.02	−0.09	−0.89	+0.009	5.62
	7.864	77.10	4.36	12.53	18.515	+0.02	−0.07	−0.32	−0.013	5.62
γ-Phenoxybutyronitrile	7.704	74.36	6.84	10.23	19.578	−0.13	−0.04	+0.30	−0.072	8.70
	7.009	74.46	6.82	9.44	17.872	−0.03	−0.06	−0.50	−0.004	8.70
p-Nitrobiphenyl	6.859	72.32	4.64	16.40	15.278	−0.01	+0.08	+0.33	+0.020	7.04
					Mean	−0.03	−0.03	−0.15 ±0.13	−0.016 ±0.009	

Summary

The method for the direct simultaneous microdetermination of carbon, hydrogen, and oxygen has been extended to include substances which also contain nitrogen.

The hypothesis is advanced that in the combustion of nitrogen-containing compounds the nitrogen is split out, during the thermal decomposition of the substance, in the form of simple nitrogen containing products which then undergo oxidation, forming, under the conditions existing in the combustion tube, only nitrogen peroxide and nitrogen. The ratio of these products formed is a function of the manner in which the nitrogen is linked in the compound. The ratio for amines and amides was found to be 26 per cent nitrogen peroxide and 74 per cent nitrogen; for nitriles, nitro, and heterocyclic nitrogen compounds, 59 per cent nitrogen peroxide and 41 per cent nitrogen.

The mechanism of the reaction between nitrogen peroxide and lead peroxide, under the conditions generally used in microcombustions, has also been studied, and the details will be reported later.

The data show that this method is capable of directly determining oxygen in nitrogen-containing substances with a mean accuracy of about 0.2 to 0.3 per cent, although individual determinations may differ from theory by more than these amounts.

Errors in the oxygen determination are largely due to errors in the carbon-hydrogen determination. As has been previously pointed out, errors made in the determinations of these elements are multiplied by rather large factors. This is particularly true of errors made in the determination of hydrogen. The determination of the oxygen consumed can be made with considerable accuracy.

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A Fatigue Cracking Test for Tire Tread Compounds

Some of the Laws of Fatigue

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An important factor in the service rendered by a tire tread is its ability to resist cracking. Cracking of tire treads in service may be classified into two kinds or phases—the initiation or start of cracks, and the growth of cracks or cuts once started—and the two phases must be differentiated. Nearly all tires in service soon develop small cracks or "checking" due to the action of ozone in the atmosphere (*9*), and may suffer cuts due to sharp objects on the road. In many cases such cuts and ozone cracks may be harmless, but if the cracks grow too rapidly they will extend to the carcass before the tire is worn out (*4*). We define the growth of cracks under the influence of mechanical action as fatigue cracking.

The quality of rubber in respect to its resistance to fatigue cracking can be improved by addition of antioxidants (*3*, *7*), and by such factors as the proper choice of accelerators (*4*), the proper balance of fillers (*1*, *3*), and the proper cure. The quantitative evaluation of such chemicals and compounding ingredients in the laboratory depends upon the validity and precision of a test. It is the purpose of this paper to describe a laboratory test which has been found to correlate with shoulder cracking in tires, and to present data from which certain laws of fatigue cracking have been deduced.

In general, a laboratory test to be valid for the prediction of service should give results in agreement with those obtained in service, and should be reproducible. A laboratory fatigue cracking test for tire tread stocks should simulate service by measuring the rate of growth of cracks after their initiation (*4*), should operate between constant strain limits rather than constant stress limits (*3*), and should be capable of operation within the range of strains actually encountered in tires. The cracks should occur in a definite region on the test piece, and the mechanism of their growth should be of the same nature as in tires. The ratings should be quantitative. For the laboratory study of tread compounds the test specimens should be easily, accurately, and cheaply prepared. A large number of samples must be tested simultaneously. The test should be fairly rapid.

A number of laboratory cracking tests have been described in the literature, but none meets all the above-mentioned conditions.

The test herein described consists of starting cracks in a grooved, molded test specimen by means of ozone; causing the cracks to grow by bending the test specimen through repeated cycles of strain with a suitable machine; and estimating the degree of cracking from the loss of bending moment

as measured in a suitable apparatus. The test meets most of the conditions outlined above. The cracks are produced in much the same way as in service, and the cracked specimens have the same appearance as do cracked tires. The method of rating the cracking is independent of any judgment on the part of the operator, and the test does not require close attention.

The chief disadvantage of the test is that it is slow compared with some other laboratory tests (*1*, *8*), for the flexing machine cannot be operated at the very high speeds of which some other machines are capable. When the tests are run at low strain limits they may last several weeks, but in such cases it is believed that what is lost in time is gained in validity. In certain cases, the time required for a test may be reduced by working to high strain limits or by running the test at elevated temperatures.

One of the reasons for using rubber in tires is its unusual resistance to fatigue. The quantitative measurement of resistance to fatigue cracking is therefore of importance as an aid in the development of tread compounds and in tire design.

A new laboratory test for evaluating the resistance to fatigue cracking of tire tread stocks is described. The precision of the strain cycle, the quantitative measurement of the degree of cracking, and the initiation of the cracks with ozone are novel features which enhance the validity of the test.

Data are given which show that ozone cracking and fatigue cracking are additive, that the rate of growth of cracks is a function of the maximum strain, that endurance limits may exist, and that the addition of antioxidants decreases the rate of growth of cracks and raises the endurance limit. The test has been found to correlate with shoulder cracking in tires.

Description of Test

Test Specimen. A diagram of the molded test specimen is shown in Figure 1.

It consists entirely of tread rubber without any fabric backing. Its essential feature is the single U-shaped groove, running across the center. The groove has a half-round bottom of 0.1588-cm. (0.0625-inch) radius, with straight sides exactly tangent, and it extends half-way through the test piece. It is important that the mold rib which forms the groove should be accurately machined and polished.

The authors have found it convenient to mold the samples in slabs about 15.8 cm. (6.25 inches) long, from which six test specimens may be cut. The test specimens are usually cut 2.5 cm. (1 inch) wide, but the exact width is not important.

Strains may be induced in the test specimen by bending it so as to open or close the groove, and the maximum surface strain always occurs in the bottom of the groove. Figure 2 shows the relationship between the angle of bend and the surface strain in the bottom of the groove of an uncracked test specimen. By "angle of bend" is meant the angle of displacement from the straight, molded shape—that is, the difference between 180° and the dihedral angle formed by the back of the test specimen. Thus, an angle of bend of 60° means that the test specimen is bent to a dihedral angle of 120°. The surface strain data shown in Figure 2 were obtained by placing short marks in the bottoms of the grooves of about 60 test specimens and measuring the lengths of the marks by means of a microscope, when the test specimens were bent to various angles in the flexing machine. It will be noted that there is a considerable variation in the measured surface strain at any given angle of bend. Some of this variation may be due to actual variations among the samples, but it is believed that most of the variation is due to errors in the measurements. The authors have observed no systematic variations in the relationship between angle of bend and surface strain for samples molded from stocks with widely differing moduli.

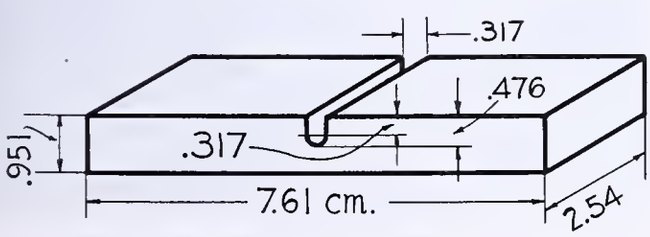

Figure 1. Test Specimen

Flexing Machine. The essential feature of the flexing machine is the mechanism pictured in Figure 3, which consists of hinged angle bars for holding the test pieces.

The test pieces fit loosely into a slot in the lower or stationary bar, and are tightly clamped to the upper or movable bar, by means of metal strips held by thumb screws. The hinges are so constructed that their axis is collinear with the approximate center-of-bend of the test pieces—i. e., the axis is 0.238 cm. (0.094 inch) in front of the faces of the back bars and in line with the centers of the grooves in the test pieces. The edges of the bars are placed 1.27 cm. (0.5 inch) apart, so that the center sections of the test pieces are left free of clamping.

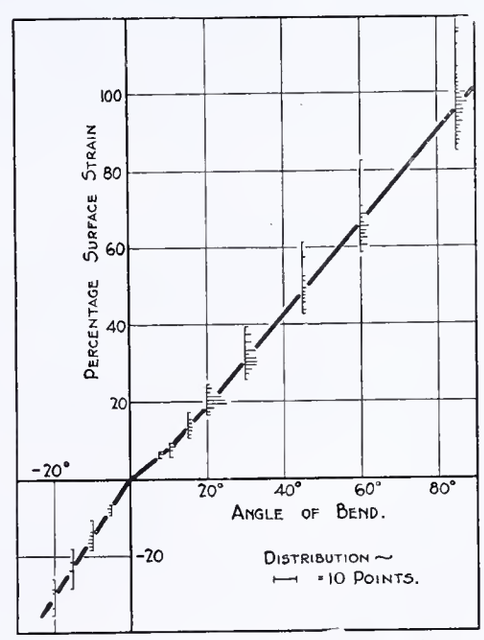

Figure 2. Relationship between Angle of Bend and Surface Strain in Uncracked Test Specimens

The position of the fixed bar is adjustable within an angle of about 90°. Through the adjustment of the throw of the crank, the movable bar may be vibrated through any angle within +45° and −45° from its central position. Thus the angle of bend to which the test pieces are to be submitted may be varied through large limits.

To develop fatigue cracking in the test pieces, the movable bar is vibrated by driving it with any suitable mechanism. One mechanism consists of a slide driven by an inverted

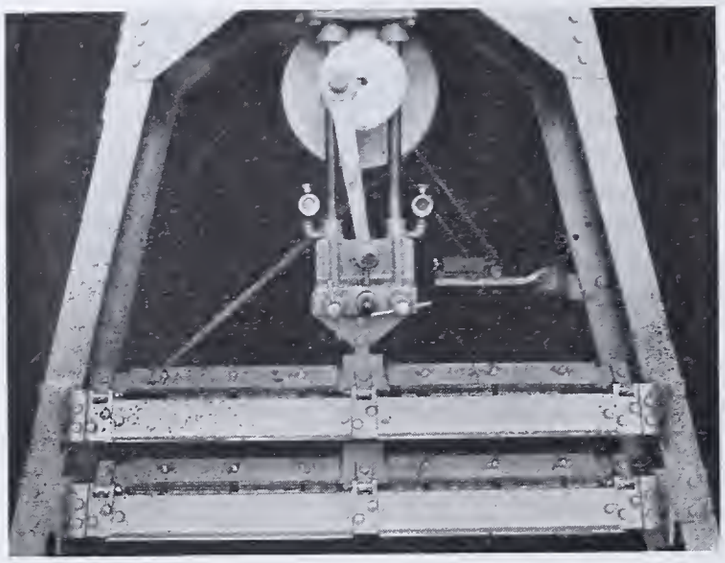

FIGURE 3. FLEXING MACHINE

DeMattia flexing machine, as shown in Figure 3. In another type of machine a simple system of levers driven by a cylindrical cam is used. The machines are usually run at the maximum speed at which they will run smoothly—i. e., 350 to 400 cycles per minute.

MEASUREMENT OF DEGREE OF CRACKING. The degree of cracking in a test piece at any time is determined by measuring its bending moment when it is bent to a definite dihedral angle—namely, 135°. Figure 4 shows the apparatus that is used.

It consists of a hinged clamp, one end of which is fastened to a board and the other end of which carries a pointer and is movable. The back side of the movable end is cut away so that the test piece may slip slightly and adjust itself to its natural position. The hinge is below the test piece and so placed that its extended axis would pass through the center of that portion of the test piece just under the groove. When the sample is placed as shown in Figure 4, except that the axis is in the vertical position, the pointers are brought together, and the torque or bending moment to bend the sample to a dihedral angle of 135° is read from the elongation of the spring.

The degree of cracking—i. e., the average percentage depth of cracks—is assumed to be equal to the percentage loss of bending moment, based upon the bending moment of the uncracked sample after the preliminary flexing. This assumption appears to be justified for practical purposes from the following considerations. Figure 5 illustrates the relationship between the percentage loss of bending moment (as measured at 45° bend) and the percentage depth of smooth, straight, even cuts made with a razor blade. The solid curve represents the average experimental relationship, while the dotted line shows the relationship required for equality. It will be observed that, for the cuts, the percentage loss of bending moment is usually a little greater than the percentage depth of cut. However, fatigue cracks are usually irregular and of uneven depth. For a given loss of bending moment the deepest portions of the cracks (which count most in service) are undoubtedly deeper than the even cuts. Hence for cracked test pieces the percentage loss of bending moment is probably more nearly equal to the percentage depth of cracks than in the case of the cuts. In one case the depth of a crack was measured microscopically at two points and gave percentage depths of 35 and 42, respectively. The loss of bending moment was 39 per cent.

If the bending moment is to give a definite measure of the degree of cracking, it is necessary that the modulus of the rubber should not change appreciably between the determination of the initial bending moment and subsequent determinations of bending moment. It has been found that unflexed samples are always stiffer than samples which have been flexed. The uncracked samples suffer a loss of bending moment during the first few cycles of flexing without any visible cracking, but after from 5 to 100 kilocycles (depending upon the angle of bend) the bending moment becomes constant for tests at room temperature, and there is no further loss until cracks appear. The "initial bending moment" upon which the degree of cracking is based is always taken on samples which have had considerable flexing, and in which the bending moment has become constant.

Thus it appears that for tests run at room temperature the percentage loss of bending moment gives a direct measure of the average percentage depth of cracks.

The measurement of the bending moment at a dihedral angle of 135° is more or less arbitrary, and it is likely that any angle greater than 90° could be used, so long as the same angle was used for all samples which are to be compared. The authors have chosen 135° merely because it is a convenient angle for their particular test specimen and gives reproducible values of the bending moment over a suitable range. Angles too near 180° should not be used, however, since there are small variations due to the way in which different samples fit into the clamps. At a dihedral angle of 135° such variations are of relatively small consequence, but at greater angles the relative effects would be greater.

Procedure for Testing

1. The samples are placed in the flexing machine and are flexed for 5 to 10 kilocycles if tested at a high angle of bend (85°) or for 50 to 200 kilocycles if tested at a low angle of bend (20° to 30°). This removes the stiffness from the samples and makes the bending moment reproducible.
2. The samples are removed from the flexing machine and their bending moments are measured to get the values for the uncracked samples, using the apparatus shown in Figure 4. The sample is placed in the apparatus with the groove out. The pointer is moved to an angle of about 75° and vibrated several times, then allowed to come back to about 30°, and again vibrated. Finally, the spring is stretched with one hand, while the pointer is vibrated with the other, until the pointer holds at 45°. The value of the bending moment is read from the scale.
3. It is usually well to repeat steps 1 and 2. This gives two readings of the bending moment on the uncracked samples. The average is taken as the zero load.
4. The samples are cracked in ozone as follows: They are placed in frames which hold them to a 20° bend, and are then put into an ozonized atmosphere until the entire surface of the groove is checked—covered with many very small cracks. These cracks should not be too deep, but just barely visible to the naked eye.

The samples are removed from the 20° frames and placed in

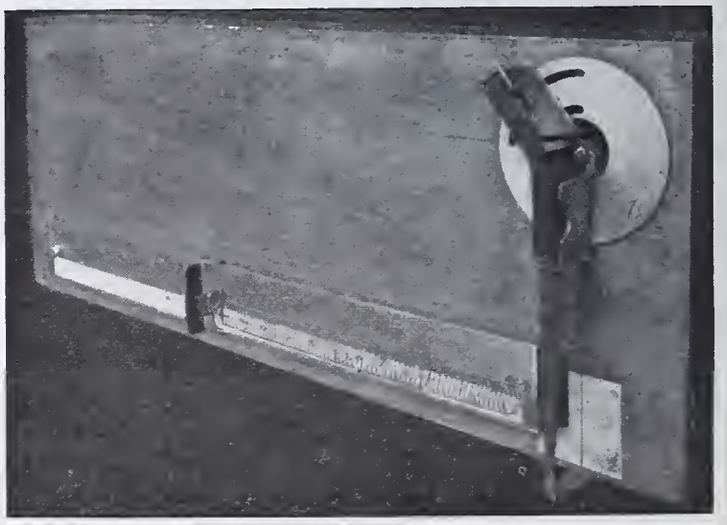

FIGURE 4. APPARATUS FOR MEASUREMENT OF BENDING MOMENT

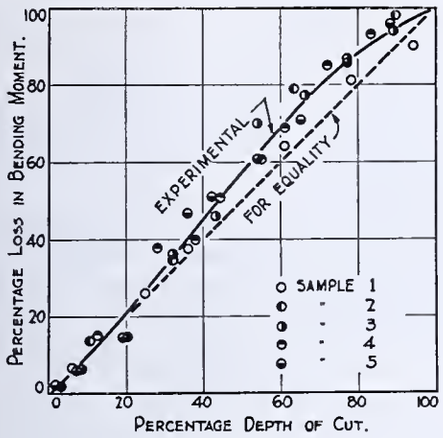

FIGURE 5. RELATIONSHIP BETWEEN PERCENTAGE LOSS OF BENDING MOMENT AND PERCENTAGE DEPTH OF CUTS OR CRACKS

frames which hold them to 7° bend. They are again put into the ozonized atmosphere until the ozone cracking is completed—that is, until the samples would show from 10 to 15 per cent loss in bending moment, which is the amount required to eliminate the induction period. (Figure 6.) A little experience will enable the operator to judge when the cracking is sufficient. When the ozone cracking has been properly done, the sample has a single broken line of ozone cracks all the way across the sample and in the bottom of the groove.

In the ozone cracking treatment the concentration of ozone is immaterial except as it determines the time necessary to get cracking. The authors prefer a low concentration, which is high enough so that the odor is very noticeable and considerably higher than atmospheric concentrations. The checking of the surface when the samples are at an angle of bend of 20° leads to a series of small cracks similar to those observed on tires in service. If this step is omitted the ozone cracks may be few and large and difficult to reproduce. For the final ozone cracking an angle of bend of about 7° must be used, so that only the bottom of the groove will suffer deep cracking. The exact amount of ozone cracking (within limits) is immaterial, since the effects of variations in the amount of ozone cracking are eliminated in the method of rating.

5. The bending moment is measured as described in step 2, from which the degree of ozone cracking may be calculated.

6. Fatigue cracking is induced in the samples by flexing them in the flexing machine. At intervals during the test the samples are removed from the machine, their bending moments are measured as in step 2, and the counter reading is recorded. The frequency at which data are taken depends upon the rate of cracking, and must be judged by the operator upon the basis of experience. In general, the intervals should be such as will give 5 to 10 per cent loss in the bending moment. For high-angle tests data should be taken about every 150 kilocycles. For low-angle tests the intervals might be 500 to 3000 kilocycles.

Rating the Samples

BY RATE OF GROWTH OF CRACKS. It has been found experimentally that, for most stocks and most flexing cycles, the rate of growth of cracks, as measured by the rate of loss of bending moment in terms of cycles of flexing, is constant up to about 60 per cent loss of bending moment. Hence the authors prefer to rate the samples in terms of $\Delta Kc/\Delta$ per cent—i. e., the number of kilocycles of flexing required to produce 1 per cent deterioration in the sample. The $\Delta Kc/\Delta$ per cent values may be calculated as follows: For each sample the bending moment data are calculated to percentage deterioration—i. e., percentage loss of bending moment, based upon the zero load values. The percentage deterioration is plotted against the total number of kilocycles of flexing, using cartesian coördinate paper. The best straight line is drawn graphically through the plots and its slope is taken as the $\Delta Kc/\Delta$ per cent value. In drawing the straight lines, points below 10 and above 60 per cent deterioration should in general be neglected.

IN TERMS OF A DEFINITE END POINT. In some cases it may be desirable to rate the samples in terms of a definite end point, such as 50 per cent fatigue cracking. The percentage deterioration values are calculated as directed above. From these values, the values for ozone cracking are subtracted in each case to give the percentage fatigue cracking. The number of kilocycles of flexing for 50 per cent (or any other degree) of fatigue cracking may be estimated by interpolation.

Characteristics of Test

INDUCTION PERIOD. When an uncracked specimen is flexed in air there is a period during which there is no loss of bending moment and no visible cracking. This may be termed an induction period. Following the induction period, cracks appear and grow at a steady rate. Curve 1 of Figure 6 shows typical data on a sample which was not subjected to ozone cracking. This curve represents a flexing test in which the strain cycle was −5° minimum bend to +60° maximum angle of bend. When the maximum bend is higher, say 90°, the induction period is shorter, both absolutely and relative to the life of the sample.

In other flexing tests which have been described (*1, 6, 7, 8*) the induction period occurs, and in general the ratings of these tests include both the induction period and the rate of growth of cracks after they form.

ELIMINATION OF INDUCTION PERIOD BY OZONE. If the cracks are initiated by the action of ozone, the induction period is eliminated, as is illustrated by curves 2, 3, and 4 of Figure 6. It is believed that for tires in service the cracks are usually initiated by the action of ozone. Often small ozone cracks may be observed on tires which have been in service only a few hours. It is partly for this reason that the authors start the cracks with ozone in their test. Initiation of cracks with ozone shortens the time of the test. Gray, Karch, and Hull (*4*) obtain a similar result with cuts.

ADDITIVITY OF STATIC OZONE CRACKING AND FATIGUE CRACKING. The effects of static ozone cracking and of fatigue cracking appear to be additive. (Figure 6.) If curves 2, 3, and 4, which represent samples in which the cracks were started with ozone, were moved along the X-axis they could all be made to coincide with curve 1, representing a sample which had no ozone cracking. This shows that cracks produced by ozone are the same in their effect as cracks produced by flexing only. Within limits, the amount of ozone cracking has no effect upon the subsequent rate of fatigue cracking.

RATE OF GROWTH OF CRACKS VS. DEGREE OF CRACKING. When the minimum strain in the flexing cycle is nearly zero, the rate of growth of cracks is nearly constant and is inde-

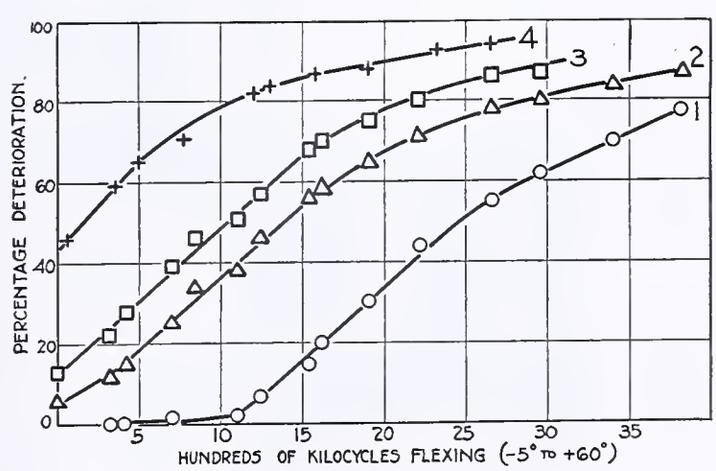

FIGURE 6. ADDITIVITY OF STATIC OZONE CRACKING AND FATIGUE CRACKING

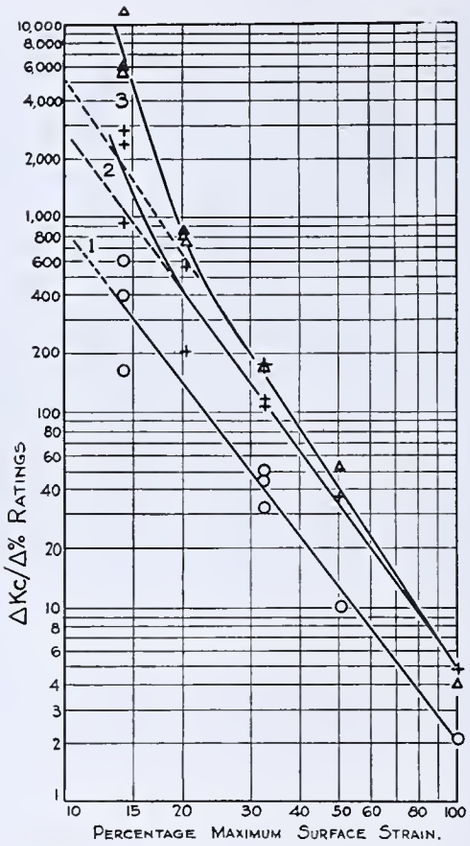

FIGURE 7. EFFECT OF MAXIMUM STRAIN

pendent of the degree of cracking, up to about 60 per cent deterioration. This is illustrated by curves 2, 3, and 4 of Figure 6 and by curves 1 and 2 of Figure 8, which are approximately straight lines within the range 15 to 60 per cent deterioration. Beyond about 60 per cent deterioration the rate of cracking decreases and tends to approach 100 per cent deterioration asymptotically. In practice, points beyond 60 per cent deterioration are usually neglected.

When the minimum strain in the flexing cycle is positive—i. e., the sample is not brought back to zero bend—the rate of cracking may not be constant during the entire life of the sample. Curves 3 and 4 of Figure 8 illustrate the progress of cracking when the angle of strain is +20° minimum to +40° maximum angle of bend.

When stocks are to be rated for their resistance to shoulder cracking in tires, the authors usually use an angle of bend of zero to a maximum. Hence for most tests the rate of growth of cracks is constant and independent of the degree of cracking, and the method of rating the samples by rate of growth of cracks applies.

Effects of Variables in Testing Conditions

EFFECT OF MAXIMUM STRAIN. When samples are cracked by flexing them between the limits zero and a maximum value of surface strain, the rate of growth of cracks is very sensitive to the value of the maximum strain. For a considerable range of maximum strain values, the following relationship holds approximately:

$$R = k/S^n$$

where R is the number of kilocycles of flexing required to cause 1 per cent deterioration in the test specimen—$\Delta Kc/\Delta$ per cent—S is the percentage maximum surface strain as measured on the uncracked specimens, while k and n are constants for any particular stock and cure.

If the values of R and S are plotted on logarithmic scales, straight-line curves are obtained, as is illustrated by the curves of Figure 7, which are straight lines from 100 per cent maximum surface strain to about 20 per cent maximum surface strain. The values of n are given by the slopes. For most stocks, n has a value of approximately +3.

The qualitative dependence of the rate of cracking upon the value of the maximum strain has been reported by other workers (*3*, *7*), but no quantitative generalizations appear to have been attempted.

EFFECT OF MINIMUM STRAIN. When samples are cracked by flexing them between the limits of a positive minimum and a given maximum strain, the rate of growth of cracks is slower the greater the value of the minimum. This is illustrated by the curves of Figure 8. Curves 1 and 2 represent samples flexed from 0° to 40° bend, while curves 3 and 4 represent samples of the same stock flexed from +20° to +40° bend. With the latter cycle the rate of growth of cracks was only about one-fifth of that obtained with the former cycle.

A similar effect has been observed by Busse (*2*) in regard to tear resistance.

It is recognized that surface strains as measured on uncracked test specimens are lower than the actual strains in the bottom of the cracks (*2*), but for cracks of any given depth and sharpness the actual strains in the cracks are probably proportional to the over-all strain in the specimen—i. e., to the measured surface strains. The true endurance limits of strain for rubber compounds would therefore be higher than those calculated, but should be proportional to the calculated values. For purposes of tire design we are limited to the over-all strains instead of the actual strains in the cracks; hence the authors measured the strains in test specimens as over-all strains in order to facilitate correlation with tires.

The knowledge of "safe limits" for tread stocks has been useful in controlling shoulder cracking in tires.

Busse (*2*) has observed a kind of endurance limit in connection with tears started from cuts. He flexed cut samples to constant maximum over-all strains, varying the minimum strains, and found that as the minimum was increased the lives of the samples became infinite. In the author's tests, however, the cracks never branch into arrowheads and grow backwards, as Busse observed with the cuts.

ENDURANCE LIMITS. Curves 3 and 4 as plotted in Figure 7 are similar in shape to the S-N curves which are plotted in the fatigue testing of metals (*5*). At low values of maximum strain, the curves depart from the straight-line relationship and tend to become parallel with the log ($\Delta Kc/\Delta$ per cent) axis. This indicates that an "endurance limit" is being approached at which the rate of growth of cracks would be indefinitely slow.

In the authors' experiments no true endurance limit was reached, for in no case was the strain so low that no cracking at all took place, but for practical purposes "safe limits" were reached in many cases. It has been calculated that for shoulder cracking in passenger size tires a rate of crack growth corresponding to a $\Delta Kc/\Delta$ per cent value of about 3500 is

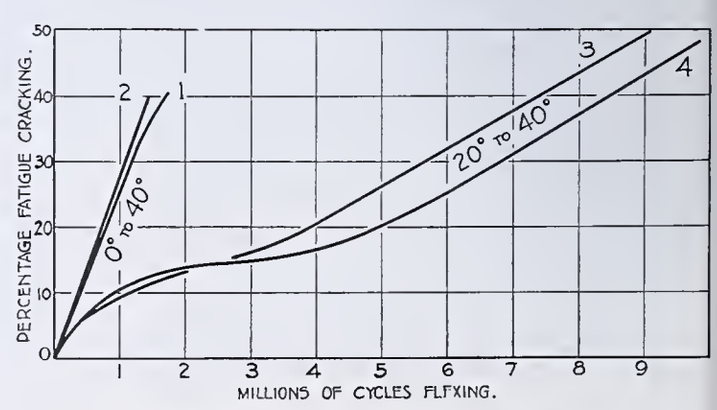

FIGURE 8. EFFECT OF MINIMUM STRAIN

safe for the life of a tire, allowing a safety factor of 5 in the rate of crack growth. The values of maximum surface strain corresponding to this safe rate of cracking may be read from curves of the type shown in Figure 7. Curve 1 represents a stock which contained no antioxidant. In this case the safe limit was not reached in the laboratory tests, but by extrapolating the curve as a straight line we would arrive at a value of about 6 per cent surface stretch. Curve 2 represents the same stock with 0.5 part BLE added. (BLE is a commercial antioxidant which is a diarylamine-ketone reaction product.) The estimated safe limit is about 12 per cent. Curve 3 represents the same stock with 1.0 part BLE added. The estimated safe limit is about 16 per cent.

Effect of Speed of Testing. The rate of cracking is measurable in terms of cycles of flexing, and when so measured is independent of the speed of the machine. This is in agreement with the observations of other workers (*7*). Also, no effects of short rest periods have been observed.

Effect of Temperature. Increasing the temperature of the air surrounding the samples always increases the rate of cracking in the authors' test. This is contrary to the observations of Somerville (*7*) who found that the rate of cracking decreased with increased temperature. His test pieces took on considerable permanent set at elevated temperatures, while the authors believe their test pieces to be fairly free from permanent set even at elevated temperatures, although other effects must sometimes be taken into consideration.

For rating shoulder cracking in tires the authors always test stocks at room temperature, about 25° C.

Effects of Variables in Stocks

Antioxidants. In agreement with other workers, the authors find that the addition of antioxidants decreases the rate of cracking. This is illustrated by the curves of Figure 6. Curve 1 is for a tread stock without antioxidant, while curves 2 and 3 are for the same stock with 0.5 and 1.0 part of BLE added. The relative effect of the antioxidant is greater at the low angle tests than at the high angle tests. The addition of antioxidant raises the endurance limit.

Cure. In tests on unaged samples at room temperature no general law for effect of cure has been observed with the authors' test. For any given stock, differences in rates of cracking among different cures are usually observed; with some stocks the undercures crack the faster, while with others the overcures crack the faster. In tests on aged samples, the overcures usually tend to crack the faster, although exceptions have been observed.

Other workers (*1*, *4*, *7*) have found that overcures crack worse than undercures.

Aging. Samples which have been shelf-aged, aged in the Geer oven, or aged in the oxygen bomb, almost invariably crack faster than the unaged samples. Other workers (*4*) have found that oven aging of tires causes them to crack more rapidly.

Precision of Test

The relative deviation from the mean of duplicate samples depends somewhat upon the angle of bend used in the test. Long-time tests run at low angles of bend are usually less reproducible than short-time tests run at a high angle of bend. In one test run at 0° to 60° bend, wherein 3 groups of 6 duplicate samples were tested, the percentage probable errors of the means were 4.48, 4.38, and 3.86 per cent, respectively. In another series of tests run at 0° to 30° and 0° to 20° bend, the average percentage probable error of the means of groups of 8 or 9 duplicates was about 25 per cent.

According to the theory of probability, it may be shown that if the difference between two quantities which are to be compared is 1.4 times the probable error of each quantity, there will be about 9 chances out of 10 that the difference is real. It follows that, if the test is capable of giving ratings for stocks with a probable error of 4.3 per cent it is capable of detecting differences in stocks of the order of 6 per cent. If the probable error of the ratings is 25 per cent, it can detect differences only of the order of 35 per cent. Differences in the rates of cracking of tread stocks as great as 500 per cent have been observed, while differences of the order of 60 per cent are not uncommon.

The variations observed with this test are not all due to errors in the cracking test itself, but may be due in large part to actual variations in the samples tested, caused by uncontrolled variables in mixing, molding, and curing.

Fatigue cracking tests are, in general, among the least reproducible of the physical tests on rubber. In order to get reliable results it is necessary to test many duplicate samples. The authors recommend testing at least 6 duplicates, and preferably more.

Correlation with Service

Analyses of data from the test have shown good correlation with tire cracking in service. Compounds which have shown up well in the laboratory test have shown less tendency to crack in tires. The test has been useful in the evaluation of such factors as antioxidants, accelerators, and softeners for their effects upon the resistance to cracking of tread stocks.

In certain cases where correlation tests have been made, the laboratory test has shown good quantitative agreement with shoulder cracking in tires. From laboratory data, together with a knowledge of the strains suffered by tire treads in service, the authors have been able to predict with fair accuracy the mileages at which troublesome shoulder cracking is likely to occur.

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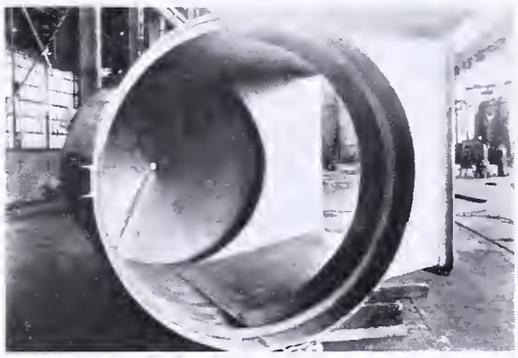

Chemical Lead-Lined Steel Stock Base, Titanium Paint Company

The Kauri Butanol Test for Solvent Power

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DURING the course of recent work pertaining to the study of hydrogenated petroleum solvents, it was necessary for this laboratory to investigate the various solvency tests for thinners used by the varnish and lacquer industry. The following solvency tests were considered: (1) kauri butanol value, (2) aniline point, (3) dimethyl sulfate value, and (4) dilution ratio.

The first three of these tests find extensive application in both the varnish and the lacquer industry, whereas the dilution ratio is restricted to the latter. Comparison revealed that although the aniline point and dimethyl sulfate tests were valuable indexes for ordinary petroleum solvents, they were inadequate for hydrogenated solvents, inasmuch as the latter are generally found to be 100 per cent miscible with dimethyl sulfate and their aniline points are much below the freezing point of aniline. The kauri butanol test and the dilution ratio were therefore the only solvency criteria suitable for the purpose.

The kauri butanol test has been used almost exclusively by this laboratory for the following reasons:

1. According to published data (*4*, pages 148 and 149) and the authors' experience, both the kauri butanol test and the dilution ratio classify petroleum solvents in the order of their aromaticity.
2. Specifications for the use of petroleum solvents as lacquer diluents (*4*, page 145) often include a minimum kauri butanol value.
3. The kauri butanol test is a more sensitive index for indicating change in aromaticity than the dilution ratio (*4*, pages 148 and 149).

Extensive investigation has been centered on the kauri butanol test in an effort to overcome some of its objectionable features and to improve upon its general reproducibility. The work is fully discussed in this paper and an improved method of standardization is suggested. The new method has been found most satisfactory and is shown to be independent of the wide variations in the composition of kauri gums used in the preparation of standard kauri butanol solution.

Kauri Butanol Test

The kauri butanol test was officially adopted in 1931 by the Paint and Varnish Superintendents' Club of the Philadelphia District (*4*). The kauri butanol value of a solvent is defined as the number of cubic centimeters of the solvent that must be added to 20 grams of the standard kauri solution at 77° F. to produce sufficient precipitation of the gum so that a printed sheet of paper (10-point print) will appear blurred and be illegible when viewed through the flask containing the solution.

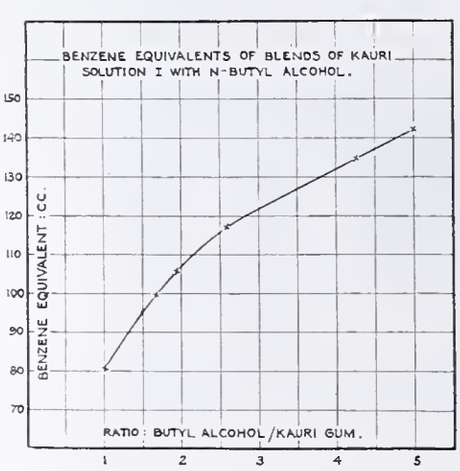

FIGURE 1

In practice the standard kauri solution is weighed into a 250-cc. flat-bottomed extraction flask. This is held by hand in a water bath kept at 25° C. (77° F.) preferably in a large crystallizing dish, the printed sheet being placed under the dish. After temperature equilibrium has taken place (about 5 minutes) the solvent is added from a buret at a fairly rapid rate until a permanent turbidity has formed. The titration is then made drop by drop to the above prescribed end point. The additional amount of solvent required to render the print illegible generally does not exceed 0.5 cc.

It is evident that, inasmuch as similar flasks are always used for the titration, the same depth of liquid will be compared for solvents of equal kauri butanol value. The magnitude of the error introduced in comparing solvents of widely different kauri butanol value due to different depths of liquid does not exceed 0.3 cc. which is smaller than the error inherent to the method. This error, moreover, will be compensated by standardizing the standard kauri solution against solvents of both high and low kauri butanol values as proposed in this paper.

The standard kauri solution is prepared by adding 100 grams of carefully selected kauri gum to 500 grams of *n*-butyl alcohol (distilling between 114.4° and 116.6° C.). The mixture is heated gently in a flask provided with a water-cooled reflux condenser, allowed to cool, and after 96 hours decanted into a clean dry bottle always kept well stoppered. While *n*-butyl alcohol of the specified boiling range has been used throughout this work (this was the material of highest purity obtainable at the time) a material boiling between 116° and 119° C. (C. P. *n*-butanol boils at 117.7° C.) is now commercially available and should be preferable.

The various factors affecting the test and the preparation of the standard solutions have been discussed at length by Beard, Shipp, and Spelshouse (*1*), who conclude that "all sources of inconsistency in results of the kauri butanol test can be easily eliminated by adopting a standard procedure, with the exception of the uniformity of the basic material, the kauri gum." These authors proposed the use of two standards, *n*-heptane and toluene; they suggested determining the curve or relationship between the toluene-heptane concentration ratio and kauri butanol value for a given kauri solution, from which the solvent power of any solvent treated with this gum solution may be expressed in terms of per cent toluene or toluene number.

The authors have been using C. P. benzene as the 100 per cent solvency standard, this procedure having been originally advocated by Kiehl (*3*). Kiehl as well as this laboratory found that the kauri butanol value of C. P. benzene or the benzene equivalent of the gum solution, as determined by the prescribed method, with standard kauri solutions prepared as specified, varied between 102 and 105 cc., depending on the grade of gum used.

To allow for this variation, data on solvents were expressed in terms of "solvent power" or the kauri butanol value multiplied by the ratio of 100 to the benzene equivalent of the gum solution used. This index should not be confused with the kauri butanol value.

Until recently it was possible to purchase kauri gum of such quality and composition that the benzene equivalents

of standard solutions did not exceed 105 cc. Now, however, for some unexplained reason, the best gum obtainable has a benzene equivalent of 113 cc., while some of the lower grades tested have values as high as 159. Table I gives the benzene equivalent of a number of samples obtained from various dealers in New York.

Table I. Benzene Equivalents of Standard Solutions Prepared with Kauri Gums from Different Sources

Sample	Type of Gum	Benzene Equivalent
		Cc.
1	Bush kauri	124.6
2	Bush dust	159.0
3	Bush dust	158.5
4	Rescraped brown chips (fossil)	152.0
5	Fossil XX	124.1
6	Fossil GXX	113.8
7	Fossil XXX	119.5
8	Fossil XXXX	123.8
9	Fossil (dark chips)	132.0
10	Fossil (light chips)	113.0
11	Fossil (small chips)	117.7
12	Fossil (superior chips)	149.5

A correction for the wide variations shown would of course be made in calculating the solvent power—i. e., its kauri butanol value divided by the benzene equivalent and multiplied by 100. However, by making determinations on a number of pure hydrocarbons it was found that even this correction does not give identical solvent power values for a given hydrocarbon in the range between *n*-heptane and benzene, when using various gum solutions. This is shown by the data in Table II, which gives the kauri butanol values and also the solvent power of six pure hydrocarbons as obtained with some of the standard kauri solutions listed in Table I.

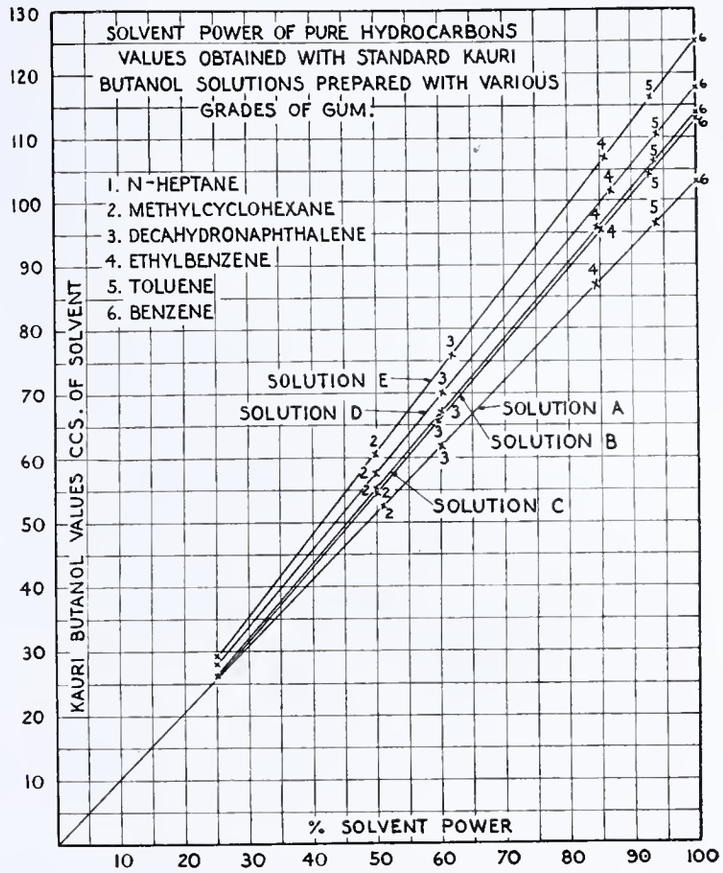

Figure 2

Table II. Solvent Power of Pure Hydrocarbons Obtained with Various Standard Kauri Solutions

	Solution A		Solution B		Solution C		Solution D		Solution E	
	Kauri butanol value	Solvent power	Kauri butanol value	Solvent power	Kauri butanol value	Solvent power	Karui butanol value	Solvent power	Kauri butanol value	Solvent power
Benzene	103.0	100.0	113.0	100.0	113.8	100.0	117.7	100.0	124.6	100.0
Toluene	96.6	94.8	104.3	92.4	106.0	93.1	110.5	93.9	116.0	93.1
Ethylbenzene	87.6	85.1	96.0	84.9	96.4	84.7	102.3	87.0	106.7	84.7
Decahydronaphthalene	62.4	60.6	65.9	58.3	66.7	58.6	70.0	59.5	75.7	60.7
Methylcyclohexane	52.5	51.0	54.4	48.3	54.7	48.1	57.3	48.7	60.1	48.2
n-Heptane	26.2	25.4	26.3	23.3	26.3	23.1	27.9	23.7	29.1	23.4

The data on solution A were obtained 2 years earlier but, inasmuch as the pure hydrocarbons used throughout these experiments are stable and were the original materials used for solution A, the results should be comparable. The benzene and toluene were C. P. materials purchased from Eimer and Amend, New York. The ethylbenzene, methylcyclohexane, and decahydronaphthalene were obtained from the Eastman Kodak Company. The boiling points of these compounds were found to check the values given in the literature. The *n*-heptane, as obtained from the California Chemical Company, had the specifications given in Table III.

Table III. Physical Constants of Normal Heptane

	Found	Literature (*2*)
Boiling point, ° C.	98.4	98.4
Freezing point, ° C.	−90.7	−90.0
Specific gravity at 20°/4° C.	0.6837	0.6840
Index of refraction n_D^{20}	1.3878	1.3850

The results given in Table II show wide variations in the kauri butanol values for a given solvent, particularly in the upper values when different gum solutions are used. The maximum variations for toluene, for instance, between solution A and solution E, is approximately 20 cc. Variations are greatly reduced, however, when data are converted to solvent power. The agreement between the results in the upper range of solvent powers is as close as may be expected for determinations made by different laboratories. The agreement is also fair in the lower ranges of solvent powers, provided the results obtained with solution A are omitted. However, the data originally published (*3*) and all the previous work were obtained with standard kauri solutions similar to solution A or of about 103 to 105 benzene equivalent. The results obtained with solutions similar to B, C, D, and E therefore must be correlated with the data previously obtained. Again, there is no assurance that the next batch of kauri gum purchased will not give a lower value. Inasmuch as the preparation of a standard kauri solution is a rather long and tedious process, it was felt that much time and effort would be saved if a method of preparing a standard solution or a procedure for standardizing the latter could be worked out to avoid these difficulties and thereby secure greater uniformity in the results.

In this direction, the authors first attempted to adjust the kauri solution by adding either additional gum or *n*-butyl alcohol to obtain a desired standard. For this purpose solutions of several concentrations were required.

Concentrated kauri solution 1 was prepared by dissolving 200 grams of gum in 200 grams of *n*-butyl alcohol; the gum used for this purpose being the same as that used in the preparation of standard solution B. Solution 2 was prepared by diluting solution 1 with *n*-butyl alcohol to the specified 5 to 1 (*4*) *n*-butyl alcohol–kauri gum ratio, without heating under reflux. Solution 3 was similar to solution 2, except that it was heated for 24 hours under a reflux condenser. Standard kauri solution 4 was prepared with kauri gum which had been dried for 12 hours at 105° C. The gum lost 2.8 per cent of its weight on drying.

The benzene and *n*-heptane equivalents of these various solutions were determined and are given in Table IV. These

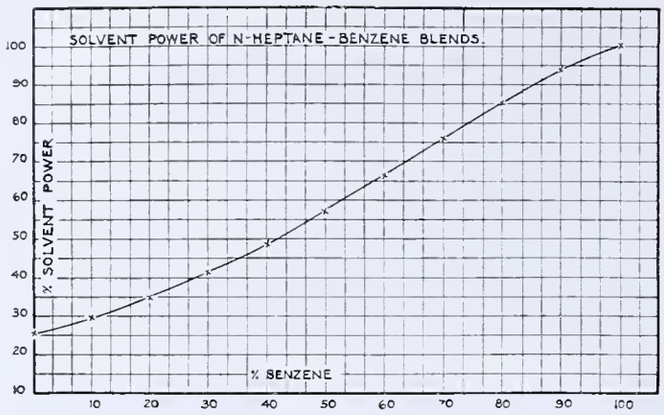

FIGURE 3

two hydrocarbons were chosen since they represent the two extremes in solvent powers.

TABLE IV. BENZENE AND *n*-HEPTANE EQUIVALENTS OF STANDARD SOLUTIONS PREPARED BY VARIOUS METHODS

Solution	*n*-Butyl Alcohol–Kauri Gum Ratio by Weight	Benzene Equivalent	*n*-Heptane Equivalent
		Cc.	*Cc.*
B	5	113.0	26.3
1	1	80.5	15.0
2	5	142.0	26.5
3	5	145.5	27.7
4	5	144.5	26.5

Table IV shows that the benzene equivalent is greatly affected by the method used in preparing the solution, while the *n*-heptane equivalent is practically independent of the method of preparation, except in the case of solution 3 where the equivalent is about 5 per cent higher. The most remarkable results are, however, the large discrepancies in benzene equivalent between the values obtained with solution B on the one hand and solutions 2, 3, and 4 on the other hand. No logical explanation for these discrepancies has been found.

To solution 1 various amounts of *n*-butyl alcohol were added and the relationship between the benzene equivalents and the amounts of *n*-butyl alcohol added plotted in order to determine the amount required to give a standard kauri solution having a benzene equivalent of as nearly 100 as possible. The results are given in Table V and the curve is shown in Figure 1.

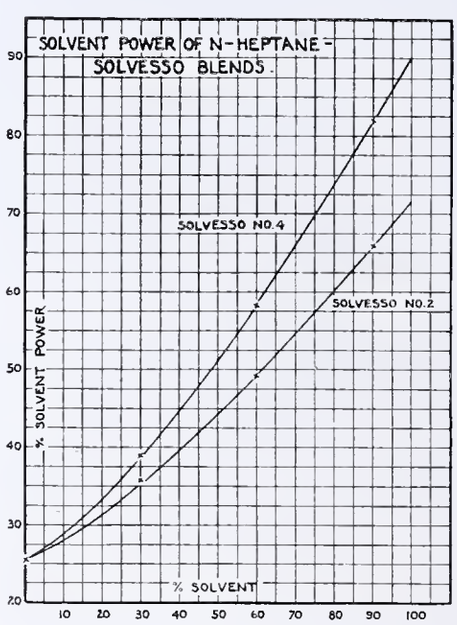

FIGURE 4

TABLE V. BENZENE EQUIVALENTS OF VARIOUS BLENDS OF KAURI SOLUTION 1 WITH *n*-BUTYL ALCOHOL

Blend	*n*-Butyl Alcohol–Kauri Gum Ratio by Weight	Benzene Equivalent
		Cc.
1	1.00	80.5
1-A	1.66	99.6
1-B	1.93	105.9
1-C	2.57	117.0
1-D	4.25	134.6
2	5.00	142.0

Solution 1-A of 99.6 cc. benzene equivalent was prepared from solution 1 by adding $33^1/_3$ per cent of its weight of *n*-butyl alcohol. The kauri butanol value of most of the various hydrocarbons listed in Table II were then determined with this solution. The results are given in Table VI. In this case the solvent powers are practically equal to the kauri butanol values, since the benzene equivalent of the standard solution is nearly 100.

TABLE VI. SOLVENT POWERS OF PURE HYDROCARBONS OBTAINED WITH STANDARD SOLUTION 5

	Kauri Butanol Value	Solvent Powers
	Cc.	%
Benzene	99.6	100.0
Toluene	91.0	91.4
Ethylbenzene	81.4	81.7
Methylcyclohexane	41.2	41.4
n-Heptane	21.3	21.4

These results are very much lower than those obtained with standard solutions listed in Table II and show that it is practically impossible to adjust a standard kauri solution to a benzene equivalent of 100 and obtain comparable values throughout. Even if satisfactory, the method would be tedious, involving at least three extra benzene and *n*-heptane equivalent determinations.

Modified Method

These difficulties have been surmounted by what is believed to be a much simpler procedure. This consists of determining the *n*-heptane and benzene equivalents of each standard solution and plotting these values against the solvent power as determined with solution A of these two hydrocarbons. A straight line is drawn between the two points from which the solvent power corresponding to any kauri butanol value (as obtained with this particular standard solution) can be directly read. The solvent powers obtained with solution A are used as standard, inasmuch as the benzene equivalent of 103.0 is close to the 104.5 cc. given by Kiehl (*3*, page 590); the *n*-heptane equivalent of 26.2 also checks the value of 26.0 found by Beard, Shipp, and Spelshouse (*1*); and moreover the curve drawn through these points passes through the origin.

Solvent power of various solvents determined with gum solutions listed in Table II interpolated from the curve, as compared with values calculated in old way, are given in Table VII and illustrated graphically in Figure 2.

The solvent powers obtained from the curves using solutions B, C, D, and E agree more closely with the data obtained with solution A than do the calculated results. This agreement is particularly apparent in the lower ranges, as for instance, for methylcyclohexane. The maximum deviation from the standard values is given by solution B for toluene and amounts to 2 per cent. The average deviation is about 1 per cent, which is considered to be within the limits of error for this type of determination.

An additional test of this procedure was made by checking the solvent power curve of *n*-heptane–benzene blends. This curve was determined in 1932 by this laboratory, using standard solution A and again recently with solution B. The results are given in Table VIII.

Table VII. Solvent Power of Pure Hydrocarbons Obtained with Various Standard Kauri Butanol Solutions

Hydrocarbons	Solution A Calculated	Solution A From Figure 2	Solution B Calculated	Solution B From Figure 2	Solution C Calculated	Solution C From Figure 2	Solution D Calculated	Solution D From Figure 2	Solution E Calculated	Solution E From Figure 2
Benzene	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Toluene	94.8	94.8	92.4	92.8	93.3	93.9	93.9	94.0	93.1	93.5
Ethylbenzene	85.1	85.1	84.9	85.5	84.7	85.0	87.0	85.8	84.7	86.1
Decahydronaphthalene	60.6	60.6	58.3	59.7	58.6	60.0	59.5	60.5	60.7	61.7
Methylcyclohexane	51.0	51.0	48.3	49.8	48.1	49.8	48.7	49.9	48.2	49.8
n-Heptane	25.4	25.4	23.3	25.4	23.1	25.4	23.7	25.4	23.4	25.4

Table VIII. Solvent Power of *n*-Heptane–Benzene Blends (by Volume)

Blend *n*-Heptane %	Blend Benzene %	Solution A Kauri butanol value	Solution A Solvent power	Solution B Kauri butanol value	Solution B Solvent power
0	100	103.0	100.0	113.0	100.0
20	80	87.5	85.0	95.6	85.2
40	60	68.0	66.0	73.3	66.0
60	40	49.7	48.2	51.8	47.4
80	20	36.0	35.0	37.1	34.5
100	0	26.2	25.4	26.3	25.4

Results with both solutions show very good agreement, the widest variation amounting to 0.8 per cent for the 60 per cent *n*-heptane blend.

The kauri butanol values of certain hydrogenated products which contain some hydronaphthalene cannot be determined directly. This is caused by the fact that the gum, at the end point of the titration, precipitates very slowly in the form of a transparent gel and therefore the prescribed end point in this method is not applicable. The solvent power of such products can be found only by determining the solvent power curve of a number of blends with *n*-heptane and obtaining the data for the pure solvent by extrapolation.

The accuracy of this extrapolation method is shown by the results obtained with two hydrogenated solvents, Solvesso No. 2 and Solvesso No. 4. The solvent power curves of *n*-heptane blends with both solvents are shown in Figure 4 and the values given in Table IX, which shows a comparison of the solvent power of Solvesso No. 2 as directly obtained and also as found by extrapolation from the blending curve. The solvent power of Solvesso No. 4, however, can be obtained only by extrapolation and is included here only as a typical example.

Table IX. Solvent Powers of *n*-Heptane and Solvesso Blends

Blends *n*-Heptane %	Solvesso No. 2 %	Kauri Butanol Value	Solvent Power
Benzene equivalent of standard solution, 113.8 cc.			
0	100	80.4	71.8[a] 71.6[b]
10	90	73.7	65.8
40	60	54.0	49.0
70	30	38.3	35.7
100	0	26.3	25.4
Solvesso No. 4			
Benzene equivalent of standard solution, 113.8 cc.			
0	100	No end point	90.3[b]
10	90	92.9	82.0
40	60	64.7	58.2
70	30	42.1	38.9
100	0	26.3	25.4

[a] Obtained by direct determination.
[b] Obtained by extrapolating the solvent power curve.

Inasmuch as the pure paraffin hydrocarbons have the lowest solvent powers as measured by aniline, kauri butanol value, or dimethyl sulfate value, it is very unlikely that commercial solvents will have solvent powers lower than that of *n*-heptane. For this reason the position of the curve lower than 25.4 per cent solvent power has not as yet been investigated by the authors.

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A Simple Automatic Cut-Off for Electric Stills

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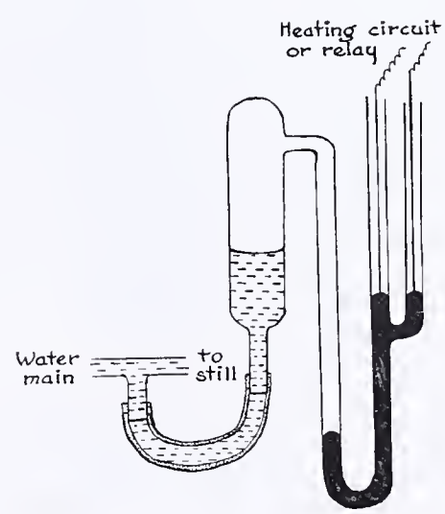
INTERMITTENT water supply in laboratories often causes the burning out of the electric heating unit of the apparatus for distilling water. An automatic cut-off, supplied by the manufacturers of a certain still and involving the use of a float actuating a mercury switch, failed to work after use for a few months and caused in this laboratory the loss of the heating units of two stills. The stills are now fitted up with the simple automatic cut-off indicated in the accompanying figure. The glass parts are made of Pyrex and the electrodes dipping in the mercury are of nickel. The device is easily constructed and has been found to be extremely satisfactory.



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Analysis of Acid Sludge from Mineral Oil Treatment

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PARALLEL to the development of scientific research in the petroleum industry has been work on refining wastes, the most important of which are perhaps the acid sludges after mineral treatment. With regard to the product obtained, the proposed and patented methods of acid sludge utilization can be divided into regeneration of sulfuric acid, obtaining of fuel and oil, production of asphalt and tar, and separation of sulfonic acids and their derivatives (*14*).

The acid sludge treatment for sulfonic acid recovery has been developed only in recent years, according to patents of Pilat and Sereda (*9*), Klipper, Suknarowski, and Chierer (*6*), and others (see literature cited in *7*, *10*, *12*, *13*). The scientific investigation of sulfonic acids was first carried out by Pilat and his collaborators (*7*, *10*, *12*, *13*).

In spite of remarkable progress in investigation and utilization of acid sludges, the literature still lacks methods of their full analysis, permitting the determination of all fundamental groups of constituents. The known methods chiefly have to do with determination of the sulfuric acid left unchanged, and moreover are not always applicable to all acid sludges.

Bacon (*1*) describes four methods of determining free sulfuric acid in light-oil sludge:

1. Gravimetric determination as barium sulfate from a water extract of a fresh sludge.
2. Methods in which the sulfuric acid is titrated with alkali under different conditions, depending upon the means of separation of the other constituents of acid sludge.
3. A method in which the heat of dilution of the sludge with water is determined and the amount of free sulfuric acid is estimated by comparison with the data on the heat of dilution of pure sulfuric acid.
4. A method in which the sludge is treated with a boiling solution of aniline in chloroform with formation of insoluble aniline sulfate, which is filtered off and analyzed for sulfuric acid.

These methods determine merely the unchanged sulfuric acid from light oil sludge, neglecting other constituents. Pilat and Starkel (*11*) determine in water solution the total acid content by titration with 0.1 *N* sodium hydroxide, and the sulfuric acid by precipitation with barium chloride. The difference between the two determinations is due to the sulfonic acids. On the same principle is based a method (*5*) which is commonly used in petroleum laboratories. According to this method, the sludge is washed with warm water and this solution is titrated on the one hand with caustic soda for free sulfuric acid and sulfonic acids; on the other hand the sulfuric acid is determined by precipitation with barium chloride, based on the supposition that barium salts of sulfonic acids are soluble in acid solution.

The sulfonic acids are obtained by difference in an amount of a few per cent, while by methods mentioned above, the amount obtained is several times greater. This discrepancy is due to the erroneous supposition regarding the solubility of barium salts of sulfonic acids (*2*); a second error arises by calculation of the sulfonic acids as sulfuric acid, whereas their molecular weight is many times higher than that of sulfuric acid. A further source of inaccuracy is the fact that acid sludge behaves variously while dissolving in water, according to the properties of oil refined and stage of treatment—whether the investigated product comes from the first, second, or subsequent portions of sulfuric acid. Thus the paraffin-base oil sludge does not dissolve entirely in water, in consequence of which the sulfonic acids occluded by hydrocarbons cannot be completely washed out; naphthene-base oil sludge dissolves readily in water, except the first and sometimes the second acid sludge, as well as the sludge obtained from very heavy stocks. This dissimilar behavior of acid sludge is probably the reason why Gurwitsch (*3*) calls Seidenschnur's data on complete solubility of sludge in water "*höchstmerkwürdig*."

According to Chierer and Primost (*2*) sodium chloride precipitates sulfonic acids, which permits their separation from sulfuric acid; on the other hand Pilat and Sereda (*8*) state that sodium chloride does not precipitate all sulfonic acids.

The method outlined below is in general applicable to all kinds of acid sludge, including products obtained from both paraffin-base and naphthene-base oils, treated with diluted, concentrated, or fuming sulfuric acid. The method permits the separation and determination of neutral constituents (oil-dissolved, and oil polymerization, condensation, and oxidation products), sulfonic acids, insoluble parts, and remaining free sulfuric acid.

The principle of distribution is based on benzene application as a solvent for neutral constituents (after previous sludge neutralization) and the use of amyl alcohol for sulfonic acid extraction from acid solution, the unchanged sulfuric acid remaining in the aqueous solution.

The course of analysis is as follows:

About 20 grams of sludge are weighed into a 300-cc. Erlenmeyer flask and a 25 per cent sodium hydroxide solution is added, until the reaction becomes strongly alkaline. Usually 100 cc. of caustic soda solution will be sufficient. Then 50 cc. of benzene and 20 cc. of alcohol are added and the mixture is refluxed until solution is complete. (If the sludge is easily soluble in water, refluxing becomes superfluous and complete dissolving will be accomplished by stirring. In case of failure to dissolve, which sometimes takes place with paraffin-base oil sludge, the dissolved part is decanted and the rest is boiled for the second time with diluted caustic soda and benzene. Sometimes boiling will be unnecessary and careful mixing with water will be sufficient.)

Mineral Oil

After the sludge is completely dissolved, the contents of the flask are poured into a 1000-cc. separator through a funnel, adding the benzene and water used for flask washing, and then carefully stirred. A few minutes later the mixture forms two layers. The lower is poured into another 1000-cc. separatory funnel, together with the middle layer which sometimes forms (sodium salts of sulfonic acids, readily soluble in water). The alkaline aqueous solution is extracted several times with benzene until the extract becomes almost colorless, and the benzene extract is added to the upper benzene layer. The collected benzene portions are washed again with hot water until the alkaline reaction disappears, and the wash water is added to the primary alkaline solution. To break an emulsion sometimes arising when benzene is washed with water, a small quantity of alcohol is added or the emulsion warmed. The benzene solution is filtered off through a dried and weighed filter. After the benzene is distilled the residue is dried at 105° C. to constant weight, with an accuracy of 0.01 gram.

Sulfonic Acids

The alkaline solution being extracted with benzene is strongly acidified with concentrated hydrochloric acid and shaken out several times with amyl alcohol till appearance of a yellowish coloring, dissolving all the sulfonic acids and small quantities

of sulfuric acid. The amyl alcohol used was a pure commercial product. To remove the small amount of sulfuric acid, the amyl alcohol solution is washed with a little water until the water begins to appear colored, when the sulfonic acids might on further washing pass into the aqueous solution. The wash water is added to the main aqueous layer. The washed alcohol solution is filtered through a dried and weighed filter into a weighed flask and the amyl alcohol is distilled off under diminished pressure from an oil bath at 100° C. The flasks used for distillation should be fitted with interchangeable stoppers (Fr. Greiner flasks). After distillation the residue is dried one hour *in vacuo* at an oil bath temperature of 115° C. having in mind that according to Pilat, Sereda, and Szankowski (*8*) sulfonic acids visibly decompose above this temperature. After drying, the flask is washed on the outside with gasoline to remove oil and weighed.

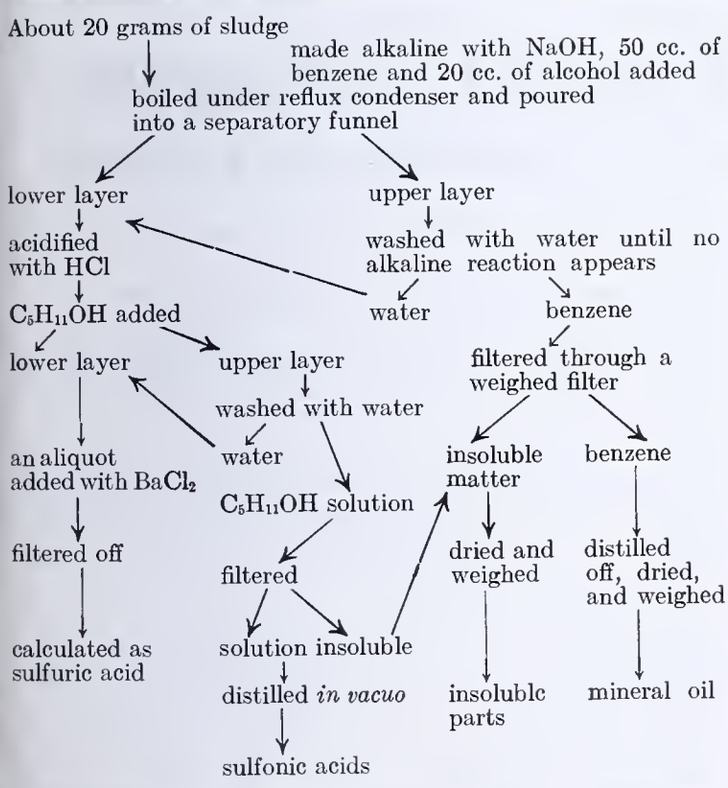
Insoluble Matter

The insoluble parts of sludge are obtained by weighing the dried filtrate from the benzene and amyl alcohol filtering.

Sulfuric Acid

The remaining acid is made up to a known volume, usually 1000 to 1500 cc., and an aliquot (25 cc.) is taken for sulfuric acid determination by precipitating with barium chloride.

An outline of the method is given below:



Tables I, II, and III give results of sludge analyses carried out by means of the method elaborated by the writers. To check the validity of the method two parallel determinations of each sludge were conducted, while control determinations were performed by Miss Geschwind.

The sulfonic acids separated by the authors by means of amyl alcohol may be divided according to Pilat and collaborators (*7, 10, 12, 13*) into at least two species, differing in solubility of their calcium salts. The sulfonic acids called by them γ-acids give calcium salts soluble in water and insoluble in ethyl ether; the calcium salts of α-sulfonic acids are insoluble in both water and ether.

To conduct this distribution, the sulfonic acids separated in the manner described above are dissolved in a small quantity of water and lime-water is added until the reaction is alkaline to phenolphthalein. (The transition is immediately visible, because the acid solution changes in alkaline medium from dirty green to brown.) To the alkaline solution amyl alcohol is added and stirred carefully in a separatory funnel. After settling and clarifying two layers form, while calcium salts, insoluble in both water and amyl alcohol, separate as a solid in amyl alcohol on the border of the lower water layer. From this lower water solution, after evaporating in a dry and weighed beaker and drying at 130° C. to constant weight, water-soluble salts are obtained, called by Pilat γ-sulfonic acids. The alcohol layer is filtered through a glass filter which has been dried at 130° C. and weighed, and is washed with amyl alcohol. This glass funnel-filter with the sediment is dried at 130° C. to constant weight to obtain the calcium salts of sulfonic acids, insoluble in both amyl alcohol and in water. Unlike free sulfonic acids, the salts are more stable and decompose at 180° C. (*7, 10, 12, 13*). The calcium salts soluble in amyl alcohol and insoluble in water are determined last by distilling off the amyl alcohol and drying the residue at 130° C. to constant weight.

Table IV gives the separation of sulfonic acids obtained by analysis II.

The water-insoluble salts are noncrystalline and dark in color when dry; water-soluble calcium salts are brown.

TABLE I. SLUDGE ANALYSES

(Second acid sludge from a naphthene-base transformer oil)

	Test I (20.78 grams)		Test II (24.65 grams)	
	Grams	*Per cent*	*Grams*	*Per cent*
Mineral oil	3.20	15.41	3.86	15.65
Sulfonic acids	7.70	37.05	9.17	37.20
Sulfuric acid	9.458	45.51	11.289	45.79
Insoluble matter	0.0214	0.10	0.0258	0.10
Total	20.379	98.07	24.34	98.74

TABLE II. SLUDGE ANALYSES

[Acid sludge from treatment with oleum (20 per cent SO_3) of a stock of specific weight d/15, 0.917; viscosity at 20° C., 7.18° E.; pour point, −48° C.; flash, 162° C.]

	Test I (20.10 grams)		Test II (21.33 grams)	
	Grams	*Per cent*	*Grams*	*Per cent*
Mineral oil	0.95	4.69	0.95	4.46
Sulfonic acids	12.70	63.18	13.79	64.65
Sulfuric acid	5.801	29.29	6.312	29.57
Insoluble matter	0.019	0.09	0.018	0.08
Total	19.47	97.25	21.07	98.76

TABLE III. SLUDGE ANALYSES

(First acid sludge from treatment of a paraffin-base stock of: specific weight d/15, 0.925; viscosity at 50° C., 4.31° E.; pour point, 0° C.; flash, 203° C.)

	Test I (20.51 grams)		Test II (19.79 grams)	
	Grams	*Per cent*	*Grams*	*Per cent*
Mineral oil	12.13	59.19	11.85	59.83
Sulfonic acids	3.67	17.89	3.27	16.52
Sulfuric acid	4.264	20.78	4.063	20.54
Insoluble matter	0.330	1.61	0.331	1.67
Total	20.39	99.47	19.52	98.56

TABLE IV. SEPARATION OF SULFONIC ACIDS

(Sulfonic acids taken for analysis, 13.79 grams)

	Calcium Salts		
		Sulfonic acids	Sludge
	Grams	%	%
Soluble in water	3.125	22.66	14.65
Soluble in amyl alcohol	11.29	81.87	52.93
Insoluble in amyl alcohol	0.584	4.24	2.74
Total	14.999	108.77	70.32

Water Determination

In the sludge analysis given above, the water content was not taken into consideration. It was found by the authors that in this case the Holde (*5*) xylene method is of no use because, when sludge is heated with xylene, the sulfuric acid acts as a strong oxidant with separation of water and sulfurous

anhydride. Then a considerable amount of water is formed from sulfuric acid decomposition and oxidation of organic substances (*4*).

The acid sludge (Table II) of 29.29 per cent free sulfuric acid content showed after heating with xylene 28 per cent water, with almost complete decomposition of sulfuric acid, as is indicated by 0.136 per cent of sulfuric acid left after heating. Otherwise if the same sludge is previously neutralized by mixing 100 grams of dry anhydrous sodium carbonate with 25 grams of acid sludge, only 7.2 per cent of water is obtained after distillation with xylene—i. e., the water included by the acid and arising from acid neutralization.

For lack of a method of water determination in acid sludge, the water content was not taken into consideration in the present determinations, but further work is to be done in this connection.

In working out a method of sludge analysis as complete as possible, the authors neglected also the small amounts of sulfurous anhydride.

A difficulty in the described method involves the removal of the final traces of amyl alcohol owing to the instability of sulfonic acids, which gives higher results for sulfonic acids.

Acknowledgment

The authors acknowledge their grateful indebtedness to Miss O. Geschwind for conducting control analyses.

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Determination of Protein Nitrogen

Accelerating the Kjeldahl-Gunning-Arnold Digestion by Addition of Phosphates

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ALTHOUGH the official (*1*) Kjeldahl-Gunning-Arnold method for protein nitrogen gives good results, it requires a long digestion period, especially if the source of heat is not entirely adequate. Various rapid methods of digestion have been reported.

Mears and Hussey (*13*) and Bimmerman and Frank (*2*) used perchloric acid to accelerate the Kjeldahl digestion. Kleeman (*9*) and Heuss (*8*) found that 25 ml. of 30 per cent hydrogen peroxide added to 1-gram samples of plant or animal material before addition of sulfuric acid shortened the digestion period.

Sborowsky and Sborowsky (*22*) and Richards (*19*) reported more rapid digestion of carbonaceous matter by substitution of mercurous iodide for mercuric oxide. Hassig (*7*) found no acceleration by the use of mercurous iodide and reported that its use is disadvantageous because of the sublimation of iodine on the neck of the flask. Parri (*16*) obtained more rapid clearing of the solution when a mixture of vanadium pentoxide and cupric oxide was used than when either of these catalysts was used alone. Lepper (*12*) used 5 grams of copper sulfate, 15 grams of potassium sulfate, and 20 ml. of sulfuric acid. He reported clearing of the solution for 1-gram sample of feeding stuff in 15 minutes and complete digestion in 45 minutes.

Lauro (*11*) substituted selenium oxychloride for mercury and obtained digestion of 1-gram samples of cereals in 12 to 55 minutes. Sandstedt (*21*) and Rich (*18*) also reported rapid digestion and satisfactory results using selenium or its compounds as catalyst. Messman (*14*) obtained digestion in 20 minutes, using mercury and selenium together as catalysts on a 550-watt electric heater. Osborn and Krasnitz (*15*) found no more rapid digestion using selenium as a catalyst than when using mercury but advise a combination of selenium with either mercury or copper; later they advised the combined use of selenium and mercury. They analyzed a wide variety of materials for nitrogen and obtained a 25 per cent saving of time over the use of mercuric oxide alone. Davis and Wise (*3*), after a survey of cereal laboratories, concluded that selenium as a Kjeldahl catalyst does not appear to be as universally adaptable to general laboratory conditions as does mercury, and its use in combination with common catalysts, especially mercury, is to be discouraged. Snider and Coleman (*24*) found that selenium, as a Kjeldahl catalyst, gave low results, caused undue frothing, and produced obnoxious odors. Clearing of the solution took place rapidly, but this was no indication of complete digestion.

Harrel and Lanning (*6*) found that, for a given heat source, the time required for complete digestion can be varied by changing the ratio of sodium sulfate to acid. Low protein results, they believe, can be explained by failure to use sufficient sodium sulfate.

Pickel (*17*) obtained digestion of miscellaneous materials by the Kjeldahl-Gunning-Arnold method in 30 minutes using the full flame of a Bunsen burner. Shedd (*23*) stated that complete digestion by the Kjeldahl-Gunning-Arnold method may be obtained in 20 minutes over a grid burner, provided mercury, not copper, is used as the catalyst.

Robinson and Schellenberger (*20*) added a gram of potassium persulfate to their microdigest to complete the digestion of cereal products in a short time. Folin and Wright (*4*) used a mixture of phosphoric and sulfuric acids with mercury and ferric chloride as catalysts in the digestion of urine. Kuehl and Gottschalk (*10*) used 15 ml. of a mixture of 100 grams of phosphorus pentoxide to 200 grams of sulfuric acid to digest 1 gram of feed in 15 to 17 minutes. Potassium sulfate and mercury were added to hasten the reaction. Guillemet and Schell (*5*) used 4 ml. of sulfuric acid and 10 drops of glacial phosphoric acid for the microdetermination of protein in cereal products. In the following work potassium phosphate or equivalent reagents are substituted in part for sodium sulfate in the Kjeldahl-Gunning-Arnold digestion.

Experimental

Samples of mixed feed, wheat products, pasture grasses, poultry feces, dried blood, fish meal, soy-bean meal, and dried skim milk were digested in duplicate by phosphate modifications of the Kjeldahl-Gunning-Arnold method and at the same time duplicate determinations were made by the official (*1*) Kjeldahl-Gunning-Arnold method. Blank determinations for the two methods were the same. Distillations were made on an electric still equipped with block tin condensers. The standard acid and alkali used were 0.1142 *N*. One milliliter of the standard acid is equivalent to 1 per cent of protein

(factor 6.25) when a 1-gram sample is used. Milliliters of acid multiplied by 0.16 give per cent of nitrogen.

Replacing Sodium Sulfate Completely by Potassium Phosphate. Two grams of mixed feed were placed in a 500-ml. Kjeldahl flask and 12 grams of dipotassium phosphate trihydrate or 10 grams of the anhydrous salt, 0.7 gram of mercuric oxide, and 0.3 gram of copper sulfate were added. The salts were well mixed with the feed, 25 ml. of concentrated sulfuric acid were then added, and the flask was well shaken. Heating and charring occurred. The flask was placed over the full flame of a Bunsen burner. Vigorous digestion took place immediately, almost filling the flask with froth, but this seldom reached the neck of the flask. Clearing took place in about 20 minutes and digestion was continued for another 20 minutes.

Analyses are reported in Table I. Clearing time was decreased appreciably by use of the phosphate, but low results were obtained on replacing sodium sulfate completely by 10 grams of potassium phosphate when compared with the official (*1*) method.

Table I. Protein Determinations on Mixed Feeds

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with K_2HPO_4 and H_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
482	19.40	0.05	19.28	0.15	−0.12
483	20.98	0.05	20.83	0.05	−0.15
484	22.76	0.18	22.45	0.10	−0.31
485	21.47	0.10	21.22	0.12	−0.25
486	19.98	0.15	19.84	0.07	−0.14
487	20.87	0.10	20.72	0.04	−0.15
488	14.50	0.20	14.27	0.00	−0.23
489	20.45	0.22	20.41	0.02	−0.03
490	17.44	0.15	17.28	0.15	−0.16
491	21.87	0.10	21.58	0.12	−0.29
492	33.46	0.20	33.40	0.00	−0.06
493	20.00	0.30	19.74	0.07	−0.26
494	22.40	0.05	22.15	0.00	−0.25
495	21.79	0.02	21.26	0.12	−0.53
496	18.19	0.02	18.08	0.05	−0.11
497	19.16	0.12	19.00	0.10	−0.16
498	15.68	0.05	15.49	0.13	−0.09
499	22.08	0.05	21.97	0.00	−0.11
500	19.13	0.05	19.00	0.10	−0.13
501	15.05	0.20	14.62	0.10	−0.43
502	19.38	0.05	19.20	0.30	−0.18
503	17.76	0.02	17.53	0.15	−0.23

[a] HgO and $CuSO_4$ catalysts.

Adding Potassium Persulfate to Cleared Digest. In another series of analyses, samples of mixed feeds were digested by the mixture just described. Clearing occurred in from 15 to 25 minutes. One gram of potassium persulfate was then added and, after bringing the solutions to boiling, the heating was discontinued. The data are reported in Table II. The results are still slightly lower than those obtained by the official method and also lower than those obtained by rapid methods using potassium phosphate together with 6 grams of sodium sulfate which are later described. While clearing took place rapidly with potassium phosphate, these results seem to substantiate the findings of Snider and Coleman (*24*) with selenium that digestion is not necessarily complete when the solution becomes clear.

Table II. Protein Determination on Mixed Feeds

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with K_2HPO_4 and H_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
508	21.75	0.00	21.45	0.10	−0.30
509	19.90	0.00	19.60	0.10	−0.30
510	20.54	0.13	20.38	0.15	−0.16
511	20.03	0.05	19.80	0.00	−0.23
512	18.40	0.00	18.13	0.05	−0.27
513	20.38	0.01	20.15	0.20	−0.23

[a] $CuSO_4$ and HgO used as catalysts. 1 gram of $K_2S_2O_8$ added after clearing.

Combining Potassium Phosphate and Sodium Sulfate. Since 1 gram of potassium persulfate added to the potassium phosphate apparently did not complete the digestion, 6 grams of anhydrous sodium sulfate were added to the above to bring about more complete digestion. Although the gas supply available for this work was barely sufficient to keep the digest boiling, clearing took place on 2-gram samples in 15 to 20 minutes over Bunsen flames. One gram of potassium persulfate was then added and the boiling was continued 5 minutes more. All digestions were terminated in less than 30 minutes. The results on mixed feeds, pasture grass, and poultry feces are given in Tables III, IV, and V. They agree closely with analyses by the official Kjeldahl-Gunning-Arnold method.

A further modification of this method was also used which included the substitution of phosphorus pentoxide plus potassium hydroxide for the potassium phosphate. Phosphorus pentoxide equivalent to 10 grams of anhydrous dipotassium phosphate was added to the sample with the sulfuric acid and potassium hydroxide was then added. Two-gram samples were placed in 500-ml. Kjeldahl flasks and 6 grams of anhydrous sodium sulfate, 0.7 gram of mercuric oxide, and 0.3 gram of copper sulfate were added. Twenty-five milliliters of the sulfuric acid–phosphoric anhydride mixture, containing 16 grams of phosphorus pentoxide per 100 ml. of sulfuric acid, were added and then mixed with the sample. About 4 grams of stick potassium hydroxide were added and the flask was swirled. After the initial vigorous action ceased the flask was placed over the burner. Vigorous digestion began immediately. Using the gas flames available, clearing took place in 15 to 20 minutes and the flask was removed after 25 minutes. These results are presented in the second part of Table III.

Table III. Protein Determinations on Mixed Feeds

Sample No.	Digested with Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with H_2SO_4, K_2HPO_4, and Na_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
482	19.40	0.05	19.43	0.15	+0.03
483	19.98	0.05	21.03	0.05	+0.05
488	14.50	0.20	14.40	0.10	−0.10
508	21.75	0.00	21.60	0.00	−0.15
509	19.90	0.00	19.80	0.04	−0.10
510	20.54	0.13	20.45	0.06	−0.08
511	20.03	0.05	20.09	0.18	+0.06
512	18.40	0.00	18.39	0.13	−0.01
513	20.38	0.01	20.30	0.20	−0.08
514	19.20	0.10	18.92	0.05	−0.28
515	16.45	0.00	16.40	0.20	−0.05
516	15.75	0.00	15.72	0.05	−0.03
517	22.85	0.10	22.82	0.10	−0.03
518	19.94	0.17	20.00	0.10	+0.06
519	21.50	0.10	21.22	0.00	−0.28
520	22.73	0.25	22.73	0.05	0.00
521	18.70	0.00	18.51	0.08	−0.19
522	15.50	0.00	15.35	0.10	−0.15
523	24.00	0.10	23.90	0.00	−0.10
400	19.11	0.07	18.96	0.06	−0.15
402	16.13	0.10	16.32	0.02	+0.19
408	19.84	0.20	19.98	0.10	+0.14
410	16.38	0.08	16.21	0.11	−0.17
414	18.44	0.14	18.34	0.02	−0.10
424	16.58	0.05	16.53	0.06	−0.05
445	18.43	0.14	18.43	0.04	0.00
381	16.47	0.06	16.45	0.06	−0.02
373	15.19	0.08	15.22	0.03	+0.03
41	16.30	0.13	16.24	0.12	−0.06
23	16.44	0.05	16.39	0.05	−0.05
42	18.36	0.03	18.28	0.15	−0.08
68	17.98	0.15	17.76	0.07	−0.22
58	15.87	0.02	15.72	0.05	−0.15
46	16.31	0.01	16.16	0.01	−0.15
			Digested with H_2SO_4, P_2O_5, Na_2SO_4, HgO, $CuSO_4$, and KOH		
485	21.47	0.10	21.44	0.13	−0.03
486	19.97	0.15	19.90	0.00	−0.07
487	20.87	0.10	20.95	0.10	+0.08
488	14.50	0.20	14.40	0.15	−0.10
489	20.45	0.22	20.54	0.07	+0.09
490	17.43	0.15	17.27	0.00	−0.16
491	21.87	0.10	21.73	0.10	−0.14
494[b]	22.40	0.05	22.19	0.17	−0.21
495[b]	21.79	0.02	21.50	0.05	−0.29
496[b]	18.19	0.02	18.15	0.00	−0.04
497[b]	19.16	0.12	19.09	0.17	−0.07
498[b]	15.68	0.05	15.66	0.12	−0.02
499[b]	22.08	0.05	21.96	0.12	−0.12
500	19.13	0.05	19.13	0.05	0.00
501	15.05	0.20	14.80	0.10	−0.25
502	19.38	0.05	19.06	0.22	−0.32

[a] HgO and $CuSO_4$ as catalysts. 1 gram of $K_2S_2O_8$ added after clearing.
[b] No $K_2S_2O_8$ was added to these digestions.

Table IV. Nitrogen Determination on Poultry Feces

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with H_2SO_4, K_2HPO_4, and Na_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
50	3.92	0.03	3.88	0.02	−0.03
51	3.99	0.02	4.02	0.00	+0.03
52	3.78	0.06	3.79	0.03	+0.01
53	3.81	0.04	3.81	0.05	0.00
54	3.66	0.00	3.69	0.00	+0.03
55	3.77	0.02	3.74	0.02	−0.03
56	3.94	0.00	3.90	0.01	−0.04
57	4.08	0.01	4.05	0.02	−0.03
58	3.87	0.01	3.83	0.01	−0.04
59	4.03	0.01	4.01	0.01	−0.02
60	4.42	0.04	4.36	0.01	−0.06
61	4.06	0.04	4.04	0.02	−0.02

[a] HgO and $CuSO_4$ catalysts. 1 gram of $K_2S_2O_8$ added after clearing.

Table V. Protein Determinations on Pasture Grass

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with H_2SO_4, K_2HPO_4, and Na_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
B	27.00	0.00	26.95	0.20	−0.05
C	26.50	0.20	26.43	0.25	−0.07
D	25.18	0.05	25.35	0.20	+0.17
E	22.85	0.10	22.70	0.00	−0.15
F	21.50	0.00	21.53	0.25	+0.03
G	23.18	0.15	23.00	0.20	−0.18
H	20.17	0.03	20.15	0.00	−0.02
M	30.54	0.01	30.38	0.04	−0.16
O	29.03	0.02	28.84	0.08	−0.19
P	29.31	0.07	29.25	0.10	−0.06

[a] HgO and $CuSO_4$ catalysts. 1 gram of $K_2S_2O_8$ added after clearing.

Table VI. Protein Determination on Wheat Products

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with H_2SO_4, P_2O_5, KOH, and Na_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
30	15.32	0.00	15.21	0.02	−0.11
31	14.68	0.05	14.49	0.08	−0.19
32	14.88	0.05	14.89	0.02	+0.01
34	14.55	0.04	14.46	0.11	−0.09
35	14.09	0.02	14.00	0.07	−0.09
39	13.65	0.06	13.65	0.00	0.00
41	16.75	0.00	16.86	0.14	+0.11
42	10.15	0.00	10.21	0.08	+0.06
43	11.25	0.00	11.33	0.05	+0.08
44	13.33	0.05	13.15	0.00	−0.18
36	13.30	0.00	13.33[b]	0.00	+0.03
37	11.81	0.09	11.82[b]	0.03	+0.01
38	13.20	0.10	13.23[b]	0.05	+0.03
40	14.78	0.13	14.75[b]	0.10	−0.03
45	18.23	0.05	18.25[b]	0.00	+0.02
46	11.88	0.05	11.88[b]	0.00	0.00
25	13.10	0.10	12.93[c]	0.07	−0.17
26	12.41	0.08	12.31[c]	0.10	−0.06
27	13.45	0.08	13.43[c]	0.20	−0.02
28	15.56	0.01	15.48[c]	0.05	−0.08
29	14.27	0.17	14.12[c]	0.02	−0.15
33	13.60	0.10	13.61[c]	0.11	+0.01

[a] HgO, $CuSO_4$, and $Fe_2(SO_4)_3$ used as catalysts.
[b] K_2HPO_4 used in digestion instead of P_2O_5 and KOH.
[c] Digested in 9 minutes on glimmer heater.

Attempts were made to substitute sodium phosphate, phosphoric acid plus potassium sulfate, or phosphorus pentoxide without potassium hydroxide, in place of dipotassium phosphate. The clearing time for any such substitution was longer than where dipotassium phosphate was used. The addition of larger quantities of the potassium phosphate caused vigorous frothing, while smaller quantities resulted in slower digestion.

Another modification following Folin and Wright's (*4*) suggestion included the addition of iron to the mixture of sodium sulfate, mercuric oxide, copper sulfate, potassium hydroxide, and sulfuric acid–phosphorus pentoxide mixture. The results of the addition of iron in the form of ferric sulfate to this digestion mixture previously described, when used in the analysis of wheat, flour, and bran, are given in Table VI.

A 700-watt hot plate was used to determine the effect of more intense heat. When the flasks were placed on the preheated hot plate, clearing occurred in 4 to 5 minutes and the digestion was completed in about 9 minutes, as indicated in Table VI. The results agree well with those by the official method.

The method is also applicable to high-protein samples.

An acid mixture was made by adding 16 grams of anhydrous phosphorus pentoxide per 100 ml. of sulfuric acid in a Kjeldahl flask, cooling, and adding 16 grams of potassium hydroxide with cooling. Fifteen to twenty milliliters of this mixture were added to the sample in a Kjeldahl flask together with 6 grams of sodium sulfate and 0.7 gram of mercuric oxide. Over grid burners clearing occurred in 5 to 8 minutes and digestion was terminated at 15 minutes. Over Bunsen burners clearing occurred in 25 minutes and digestion was terminated after 45 minutes and 90 minutes to determine the effect of longer boiling. At the same time, samples were digested by the Kjeldahl-Gunning-Arnold method for 120 minutes. Results are given in Table VII.

Table VII. Protein Determination on High-Protein Materials

Substance Analyzed	Weight of Sample	Digested with Na_2SO_4 and H_2SO_4[a]: 15 minutes Grid burner	45 minutes Bunsen burner	90 minutes Bunsen burner	Kjeldahl-Gunning-Arnold Digestion: 120 Minutes Bunsen Burner
	Grams	%	%	%	%
Meat scrap	1.0	59.93	59.55	59.95	60.00
Herring meal	0.8	68.71	69.18	69.03	69.11
Mixed feed	1.0	48.23	47.75	47.90	48.00
Meat meal	0.8	56.88	56.82	57.12	56.71
Dried blood	0.8	63.20	62.40	61.94	63.19
Meat meal and bone	0.8	58.50	58.37	58.25	58.80
Herring meal	0.7	72.96	72.83	73.00	72.94
Herring meal	0.7	73.13	73.28	73.11	73.28
Soy-bean meal	1.0	47.65	47.50	47.50	47.15
Dried skim milk	1.5	36.23	36.05	36.02	36.08

[a] 6 grams of Na_2SO_4 and 20 ml. of H_2SO_4 containing 3.5 grams of P_2O_5 and 3.5 grams of KOH-HgO catalyst.

The results obtained by the rapid digestion of high-protein materials, wherein potassium phosphate is substituted in part for sodium sulfate, agree well with the longer Kjeldahl-Gunning-Arnold method. Satisfactory results were also obtained when using Bunsen flames, although a somewhat longer digestion period was required.

Discussion

The substitution of dipotassium phosphate for part of the sodium sulfate in the Kjeldahl-Gunning-Arnold protein digestion shortened the required digestion time. Using Bunsen flames total digestion time for low-protein materials was reduced to 25 minutes or less. Trials made with a 700-watt plate indicated that digestion time may be reduced to 10 minutes or less. With high-protein samples digestion was completed in 15 minutes with a grid burner. The results of analysis of mixed feeds, wheat products, pasture grasses, and poultry feces, as well as difficultly digestible high-protein material, agreed well with results obtained by the official method. The mixture served a double purpose by shortening the digestion period and at the same time furnishing a solution, the vapors from which condensed and washed the sides of the flask. The charred material carried to the top of the flask and into the bottom of the neck by rapid heating on the hot plate was washed down rapidly by condensing vapors, thus obviating the necessity of swirling the flask during digestion. The solution cooled much more without solidifying than digests using sodium sulfate.

Similar results were obtained with a sulfuric acid solution to which 16 grams of phosphorus pentoxide and 16 grams of potassium hydroxide per 100 ml. were added. When 15 to 25 ml. of this solution were added to samples, together with 0.7 gram of mercuric oxide and 6 grams of sodium sulfate, rapid digestion occurred and good results were obtained.

Low results were obtained when the sodium sulfate was completely replaced by 10 grams of potassium phosphate. The addition of iron to the catalysts and the use of potassium persulfate to complete the digestion were not shown to be necessary.

The use of phosphate partially to replace sulfate will, of course, slightly increase the cost of reagents used in the protein determination. The saving in gas or electricity during the shorter digestion period should, however, more than offset the increase in reagent cost. If anhydrous dipotassium phosphate is used, a mixture of 64 per cent dipotassium phosphate and 36 per cent sodium or potassium sulfate may be prepared and added to the sample from a dipper. When the phosphorus pentoxide–potassium hydroxide modified digestion is employed, a sulfuric acid solution containing 16 grams of phosphorus pentoxide and 16 grams of potassium hydroxide per 100 ml. may be prepared. The digestion mixtures in either case should be added to the sample not more than a few minutes before placing the flasks on the heaters.

Summary

Ten grams of anhydrous dipotassium phosphate or 12 grams of dipotassium phosphate trihydrate, or an equivalent quantity of phosphorus pentoxide plus potassium hydroxide, were substituted for ten-sixteenths of the sodium or potassium sulfate used in the digestion of samples for protein nitrogen determinations.

Two-gram samples of feeds and wheat products were digested in 25 minutes or less over the Bunsen flames available and in 9 minutes on a preheated 700-watt electric plate. Samples of dried blood, fish meal, soy-bean meal, and dried skim milk were digested in 15 minutes over grid burners. The results obtained compared well with analysis by the official Kjeldahl-Gunning-Arnold method.

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Determination of Manganese and Magnesium in Soils and Silicate Rocks

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THE methods of rock, mineral, and soil analysis commonly suggested by Hillebrand and Lundell (*4*) and the Association of Official Agricultural Chemists (*1*) require that manganese be determined on a separate portion of the sample, because of incompleteness of separation of manganese by precipitation with bromine, persulfate, and ammonium sulfide. Furthermore, because of this incompleteness of separation, Hillebrand and Lundell recommend that the magnesium, when determined, be corrected for contaminating manganese. Thus, if both manganese and magnesium are to be determined, it requires that two fusions and two determinations of manganese be made.

Since manganese may be quantitatively precipitated as manganese ammonium phosphate, and since it generally exists in soils and silicate rocks in much smaller quantities than magnesium, it appeared possible to develop a method in which the manganese and magnesium are precipitated and weighed or titrated together as the phosphate, after which the manganese is determined colorimetrically or volumetrically and the amount of magnesium obtained by difference.

Precipitation and Titration of Manganese Ammonium Phosphate

The first step in this investigation was to determine whether manganese could be completely precipitated under the same conditions as magnesium and ultimately titrated by the method developed by Handy (*3*).

Measured portions of standardized 0.05 *N* potassium permanganate were mixed with 100 cc. of 0.5 *N* hydrochloric acid and a few drops of a 1 per cent solution of oxalic acid added to bring about complete reduction. The solution was neutralized with ammonia, and 20 cc. of a 10 per cent solution of sodium ammonium hydrogen phosphate were added, followed by 10 cc. more of concentrated ammonia. The solution was then boiled and allowed to cool at room temperature overnight. After filtration, the precipitate and paper were washed with 0.5 *N* ammonium hydroxide. The filter with precipitate were removed and allowed to dry at room temperature until ammonia-free—that is, until ammonia fumes could no longer be detected with bromocresol purple test paper. The filter paper containing the precipitate was then placed in a 250-cc. flask, 50 cc. of carbon dioxide-free distilled water and an excess of standard sulfuric acid were added, the flask was shaken until the paper was pulped, and the solution back-titrated to pH 4.5, using bromocresol green as an indicator. [J. A. Chucka (unpublished data) found that bromocresol green is superior for this purpose to the indicator used by Handy.] The filter paper pulp was then filtered off and the manganese determined volumetrically, using the bismuthate method of Park (*5*). The results of this test are given in Table I.

These data indicate that manganese may be quantitatively precipitated as manganese ammonium phosphate, and this in turn titrated according to the method of Handy (*3*).

Table I. Determination of Manganese

Manganese Taken	Manganese Found by Precipitation and Titration as $MnNH_4PO_4$	Manganese Found by Bismuthate Method
Mg.	*Mg.*	*Mg.*
5.50	5.53	5.47
8.25	8.08	8.25
11.00	11.13	11.00

Table II. Determination of Manganese and Magnesium

Manganese Taken	Manganese by Bismuthate Method	Magnesium Taken	Magnesium by Difference
Mg.	*Mg.*	*Mg.*	*Mg.*
5.50	5.47	5.98	5.97
1.10	1.11	5.98	5.97

Determination of Manganese and Magnesium

Precipitation and Titration as Phosphates. Aliquots of known solutions of potassium permanganate and magnesium chloride were mixed together with 100 cc. of 0.5 *N* hydrochloric acid and the combined amounts of manganese and magnesium determined by precipitation and titration as phosphate. The manganese was then determined by Park's bismuthate method and the amount of magnesium obtained by difference. The results obtained are given in Table II, and show that manganese and magnesium may be satisfactorily determined in this way.

Determination in Solutions Containing Iron, Aluminum, and Calcium. The purpose of these tests was to determine whether there is any noticeable precipitation of manganese during the ammonia separation and the calcium precipitation as the oxalate, and, further, to compare the results for magnesium when the manganese is previously precipitated by either bromine or persulfate with those obtained by the difference method just explained.

Synthetic solutions were prepared which contained 100 mg. of R_2O_3 purified by reprecipitation, magnesium from recrystallized magnesium nitrate, calcium from calcite (free of manganese and magnesium), and manganese from potassium permanganate. The R_2O_3 was then separated from these solutions by two ammonia precipitations at pH 6.2. In two of the samples, the manganese was then precipitated as the dioxide with either bromine or persulfate, ignited, and weighed as Mn_3O_4. The Mn_3O_4 precipitates were fused with sodium carbonate and the manganese was redetermined by the bismuthate method. The calcium was separated from all samples as the oxalate at pH 4.4 according to the procedure of Chapman (*2*). The magnesium or manganese and magnesium together were then precipitated and determined by the method previously described.

The results, given in Table III, show that differences in procedure caused but slight differences in the values obtained for magnesium and calcium. However, the values for magnesium obtained by the difference method are uniformly higher. When the manganese was weighed as Mn_3O_4, high results were obtained for manganese, and when the Mn_3O_4 was fused and redetermined volumetrically, slightly low values resulted. The high values may be attributed to a contamination of R_2O_3, and low values to an incomplete precipitation of the manganese.

The magnesium precipitates obtained when the bromine or persulfate method was used for manganese gave in all cases a test for manganese.

In further tests, 1-gram samples of a soil (Miami silt loam) were treated with hydrofluoric and sulfuric acids to decompose the silicates and volatilize the silica. The residues were fused with potassium bisulfate, dissolved, and treated in the same manner as the synthetic solutions. The results are given in Table III and are in accord with those previously given. The results by the difference method are again slightly higher for both manganese and magnesium. The higher results for the manganese may be attributed to more perfect precipitation, and the lower results for magnesium in the bromine method to the possibility that sufficient ammonia salts may have been destroyed by the bromine to cause some precipitation of magnesium with the manganese dioxide.

Table III. Results with Different Procedures of Analysis

Procedure	Material Analyzed	Manganese Taken	Manganese Found Weighed as Mn_3O_4	Manganese Found Bismuthate method	Magnesium Taken	Magnesium Found	Calcium Taken	Calcium Found
		Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
Mn pptd. with Br	Synthetic solution	1.65	2.74	1.35	9.75	9.61	9.90	9.98
Mn pptd. with persulfate	Synthetic solution	1.65	2.36	1.48	9.75	9.60	9.90	9.90
Mn and Mg pptd. as phosphate, Mg by difference	Synthetic solution	1.65	...	1.63	9.75	9.70	9.90	9.95
Mn pptd. with Br	Soil	..	10.7	1.42	..	3.66	..	5.1
Mn pptd. with persulfate	Soil	..	12.5	1.43	..	3.69	..	5.0
Mn and Mg pptd. as phosphate, Mg by difference	Soil	..	...	1.53	..	3.93	..	4.9

Results for Manganese with the Two Procedures

In the direct method for manganese, 1-gram samples of a pyroxene were treated with hydrofluoric and sulfuric acids, and heated, and the residue was fused with potassium bisulfate. The fusion was dissolved in 3 *N* sulfuric acid and the manganese determined by the bismuthate method. In the second method, involving the indirect determination of magnesium, other samples of pyroxene were fused with sodium carbonate and treated with dilute hydrochloric acid, and the silica was removed after dehydration. The R_2O_3 was precipitated at pH 6.2 and filtered off, the calcium was precipitated at pH 4.4 and filtered off, and the magnesium and manganese were then precipitated as the phosphate which was ignited to the pyrophosphate form. This was fused with sodium carbonate and the manganese determined by the bismuthate method. The results are as follows: by the direct method, 0.51 mg., and by the method involving magnesium by difference, 0.48 mg. of manganese. These results agree within experimental error.

Details of Proposed Procedure

Fuse a sample of soil or mineral with sodium carbonate and remove the silica in the regular way. Precipitate the R_2O_3 with ammonia at pH 6.2 and filter off. Precipitate the calcium with oxalic acid at pH 4.4 and filter off. Remove the excess ammonia salts by evaporation with nitric acid (be careful to avoid spattering). Take up the residue with 5 cc. of concentrated hydrochloric acid diluted to 100 cc. and neutralize with ammonia. Add 20 cc. of 10 per cent sodium ammonium hydrogen phosphate solution, followed by 10 cc. excess of concentrated ammonia. Bring solution to a boil and allow to cool at room temperature overnight. Filter off the precipitate and wash with 0.5 *N* ammonium hydroxide. Remove the filter paper with precipitate, and air-dry until free of ammonia. Place the filter paper and precipitate in a 200-cc. flask, add 50 cc. of carbon dioxide-free water, and follow with an excess of standard sulfuric acid. Shake the flask until the paper is pulped, and back-titrate with standard sodium hydroxide to pH 4.5, using bromocresol green as the indicator. This titration represents the phosphate combined with manganese and magnesium.

In case large quantities of manganese are present, two drops of a 1 per cent solution of sodium oxalate adjusted to pH 4.5 should be added with the standard acid to assure complete solution, which is indicated by disappearance of brown color. Remove the filter paper pulp by filtration and determine the manganese in the solution by Park's sodium bismuthate method. Convert the manganese to equivalent value in cubic centimeters of the standard sulfuric acid and subtract this from the previous titration value, giving the magnesium by difference. When there is a large precipitate of magnesium and

manganese phosphates, it may be more convenient to ignite the precipitate to the pyrophosphates, weigh, and then fuse the pyrophosphate with sodium carbonate and proceed with the bismuthate method for manganese.

Summary

The precipitation of manganese by oxidation with bromine or persulfate in the regular course of analysis of rocks and soils has not been satisfactory because of incompleteness of precipitation of the manganese, and at times contamination of the manganese precipitate with magnesium and the magnesium precipitate with manganese. To overcome these difficulties, it is suggested that the manganese be precipitated with the magnesium as the phosphate. The phosphates of manganese and magnesium are then weighed or titrated together, after which the manganese present is determined by means of the bismuthate method, and the amount of magnesium is obtained by difference. In a number of tests this procedure has given satisfactory results.

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Refractometric Estimation of the Total Solids Content of Whole Eggs and of Yolks

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A CORRELATION between the total solids contents and the indices of refraction of whole egg and of yolk magma obtained from hens' eggs shows that an estimation of the per cent total solids may be made by the use of a refractometer. A study made at the California Agricultural Experiment Station (*1*, *3*) has shown that the total solids content of egg white may be estimated refractometrically.

In the study herein reported, the eggs were taken from carload deliveries received at an egg-freezing plant in Jersey City, from various parts of the United States during the egg-producing season of the year 1931. No storage eggs were used.

Yolks were separated from whites in commercial fashion by girls accustomed to the work of a commercial egg-breaking plant supplying bakers and confectioners with whole egg, yolks, or whites according to demand. This plant prepared commercially two types of yolks, one known as "commercial yolk" and the other as "dry yolk." In the preparation of the latter, extra care was exercised to remove as much of the egg white as was practically feasible. Consequently, all the yolk samples studied contained some adhering whites. This paper, therefore, does not attempt to record the total solids in the egg yolk entirely free from egg white but nevertheless presents a method by which such determinations may be made if desired. A method for completely separating the egg white from the yolk is given by Pennington (*4*).

The whole egg magmas were prepared in the laboratory. Two grades were studied, U. S. Extras and U. S. Standards, the selection according to grade having been made by expert egg candlers. Samples were prepared for analysis in the following manner:

Six (or three) eggs at about 5° C. were removed from the shells and then disrupted to a uniform magma by the operation of a typical malted milk mixer. (In the early part of the work a composite sample was made from six eggs, or yolks, but later the sample was reduced to three.) The yolks as received from the plant were disrupted and mixed in the same manner, in all cases, six yolks constituting one sample.

The magma was then submitted to analysis. The determination of total solids was carried out according to the Association of Official Agricultural Chemists method (*2*). The index of refraction was read in an Abbé type refractometer around the prisms of which water at 25 ± 0.01° C. was circulating. A drop or two of the remixed egg magma was pipetted onto the prism of the instrument. (Owing to danger of "creaming" of the fatty matter, the magma was always carefully mixed in the sample bottle immediately prior to placing it in the refractometer.) The prism was then closed and the index of refraction was read exactly one minute later. This procedure was adopted for two reasons, in order to allow time for temperature equilibrium and because the reading changes with time.

Egg white gives a sharp and easily read line of demarcation between the illuminated and dark segments of the field. In the case of yolk magma, the line of demarcation is less distinct, while whole egg magma in general gives a poorer boundary line than yolk magma. The distinctness varies with different specimens. However, with a little practice operators can readily learn to check each other to about 3 units in the fourth decimal place of refractive index in the case of whole egg magma and better in the case of yolk magma. A dipping or immersion refractometer was tried on yolk and whole egg magma. Owing to its greater sensitivity, the line of demarcation was too blurred and consequently this type of refractometer was found inapplicable for the purpose of this study.

Table I. Numbers of Specimens Studied

	(Spring 1931) March	April	May	June	Total
Whole egg, U. S. Extras	38	14	10	15	77
Whole egg, U. S. Standards	38	13	9	9	69
Commercial yolks	19	20	16	9	64
Dry yolks	9	17	17	9	52

The number of specimens of fresh eggs examined is given in Table I according to the months of the year they were received and analyzed. When the total solids contents were plotted against the indices of refraction, the distribution of points indicated a straight-line relationship. On the assumption of this indication, the several sets of data were subjected to mathematical analysis by the method of least squares which produced the following equations, where R equals index of refraction and S equals per cent total solids:

Whole eggs, U. S. Extras	$S = 497.0R - 658.29$
Whole eggs, U. S. Standards	$S = 439.9R - 579.49$
Commercial yolks	$S = 503.1R - 663.15$
Dry yolks	$S = 542.4R - 718.19$
All yolks (combination of data on "dry" and "commercial" yolks)	$S = 565.4R - 750.76$

After having derived these equations, the total solids content for each specimen included in the data was calculated by substitution of the observed values for R. The differences, d, between the observed and calculated values for the per cent total solids were then used to calculate the standard deviation, $S.D.$, by means of the formula $S.D. = \sqrt{\frac{\Sigma d^2}{n}}$ where n equals the number of cases, with the following results:

Whole eggs, U. S. Extras	$S.D. = \pm 0.30$
Whole eggs, U. S. Standards	$S.D. = \pm 0.31$
Commercial yolks	$S.D. = \pm 0.59$
Dry yolks	$S.D. = \pm 0.45$
All yolks	$S.D. = \pm 0.55$

The standard deviations for the yolks are seen to be higher than those for the whole eggs, despite the more distinct line between light and shadow in the refractometer observed in the case of the yolks. Thus the relationship between refractive index and total solids is more variable with yolks of commerce than with whole eggs. This is to be expected in view of the fact that the yolks measured contained variable amounts of whites.

Since a large fraction of the total solids of whole eggs and an even larger one in case of yolks is fatty matter emulsified in the continuous aqueous phase, it is remarkable that the refractometric method works at all. Since it does, there is evidently a relationship between the total fatty matter and the water-soluble matter, as is the case in cows' milk where a high fat content is accompanied by a high protein content and vice versa.

An examination of the data obtained in this study revealed an indication of a seasonal variation in the case of yolks and to a less extent in the case of whole eggs. The determined values for total solids of late June eggs were lower than those calculated by means of the equation, and to a smaller extent early March eggs showed calculated total solids lower than those actually determined. However, the number of specimens analyzed was insufficient to give more than a general trend. Further study is necessary to determine the extent of this seasonal variation.

For the benefit of those who may wish to apply the data at temperatures other than 25° C., temperature coefficients were determined by measurements upon 7 specimens of whole egg and 7 specimens of dry yolk. These showed that there is a straight-line variation between the temperatures of 20° C. (68° F.) and 30° C. (86° F.) The method cannot be applied outside of this temperature range. In the case of the refractive index of whole egg, 0.0001 should be added (or subtracted) for each degree Centigrade above (or below) 25° C. (77° F.) in order to reduce the reading to the 25° C. (77° F.) basis. The corresponding correction for dry yolk refractive index is 0.0002.

While the number of cases studied is small, the application of the equations derived from them to 1932 spring eggs and yolks gave such satisfactory results that it was decided to publish the results herein given as a rapid method for the estimation of the total solids content.

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A Short Method for Calculating Delta *D* in a Crystal Growth Process

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IN ORDER to predict the screen analysis of the product from the analysis of seed it is necessary to calculate ΔD, the increase in size of opening (mesh) through which a crystal will pass after the growing process is completed. McCabe (*2*, *3*) does this by integrating the following equation graphically:

$$W_p = \int_0^{W_s} \left(1 + \frac{\Delta D}{D_s}\right)^3 dW_s \qquad (1)$$

where
W_s and D_s give the screen analysis of the seed
W_p = weight of crystal product

Values are assumed for ΔD, a curve of $\left(1 + \frac{\Delta D}{D_s}\right)^3$ against W_s is plotted for each value of ΔD, and the area under each curve measured. The ΔD giving the proper value for W_p is then used in calculating the final screen analysis.

The purpose of this paper is to eliminate the cut-and-try graphical integration by substituting for it a rapid method of finding ΔD. The method will be illustrated by applying it to the example on the crystallization of potassium chloride worked out by McCabe (*1*).

The screen analysis of the seed (D_s and W_s) is given. Calculations made from solubility data show that 156 pounds of product will be obtained per 100 pounds of seed. From these data ΔD may be calculated as follows:

To integrate Equation 1 it is necessary to obtain an expression for D_s in terms of W_s. This is done by plotting D_s against W_s and drawing the best straight line through the points. (The straight line is an approximation, since the cumulative screen analysis plot will curve at either end, but the approximation is sufficiently accurate for practical purposes.) This will give

$$D_s = b + mW_s \qquad (2)$$

where b is the intercept on the D_s axis and m is the slope.

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For the data in the problem being considered the values of b and m are found to be 0.09 and -0.0006, respectively.

Substituting Equation 2 in 1 we obtain

$$W_p = \int_0^{W_s}\left(1 + \frac{\Delta D}{b + mW_s}\right)^3 dW_s$$

which expanded gives

$$W_p = \int_0^{W_s}\left(1 + \frac{3\,\Delta D}{b + mW_s} + \frac{3\,\overline{\Delta D}^2}{(b + mW_s)^2} + \frac{\overline{\Delta D}^3}{(b + mW_s)^3}\right)dW_s \qquad (3)$$

As a first approximation the last two terms in parentheses are negligible. Equation 3 then becomes

$$W_p = \int_0^{W_s}\left(1 + \frac{3\,\Delta D_t}{b + mW_s}\right)dW_s$$

where ΔD_t is the tentative value of ΔD. This integrates to

$$W_p = \left[W_s + \frac{3\,\Delta D_t}{m}\log_e(b + mW_s)\right]_0^{W_s} \qquad (4)$$

Solving Equation 4 for ΔD_t, changing to the common logarithms, and substituting for $b + mW_s$ the values D_{s_0} and D_{s_i}, where D_{s_0} = intercept of straight seed line at $W = 0$, and D_{s_i} = intercept of straight seed line at $W = W_s$ we obtain

$$\Delta D_t = \frac{(W_p - W_s)(m)}{6.9\log_{10} D_{s_i}/D_{s_0}} \qquad (5)$$

Substituting in Equation 5 the values for W_p, W_s, m, D_{s_0}, and D_{s_i}, we obtain

$$\Delta D_t = 0.0102$$

Since ΔD is so small, the term containing $\overline{\Delta D}^3$ may be neglected. The turn containing $\overline{\Delta D}^2$ may be considered to be only a correction factor which can be estimated by using $\Delta D = \Delta D_t$, thereby converting Equation 3 again into a linear rather than a quadratic or cubic equation. The integrated form of 3 becomes

$$W_p = \left[W_s + \frac{3\,\Delta D}{m}\log_e(b + mW_s) - \frac{3\,\overline{\Delta D_t}^2}{m(b + mW_s)}\right]_0^{W_s}$$

Solving for ΔD we obtain

$$\Delta D = \frac{m(W_p - W_s) + 3\,\overline{\Delta D_t}^2\left(\dfrac{D_{s_0} - D_{s_i}}{D_{s_0}D_{s_i}}\right)}{6.9\log_{10}\dfrac{D_{s_i}}{D_{s_0}}} \qquad (6)$$

Substituting in Equation 6 the values for m, W_p, W_s, D_{s_0}, and D_{s_i} we obtain $\Delta D = 0.009$, which is the value found by McCabe (*1*).

The steps then are as follows:

1. Plot the screen analysis of the seed and draw the best straight line through the points. This gives $D_s = b + mW_s$. Values for D_{s_0}, D_{s_i}, and m are read from this curve.
2. Obtain ΔD_t, a tentative value for ΔD, from Equation 5.
3. From Equation 6 obtain the final value for ΔD.

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Spectrophotometric Determination of Copper in Ores and Mattes

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THE colorimetric method for the determination of copper based upon the formation of the blue copper-ammonia complex ion $[Cu(NH_3)_4]^{++}$ by the addition of an excess of ammonium hydroxide to a solution of cupric ions has been known and used for many years (*2, 8*). While it has given satisfaction, it has the disadvantage of requiring the preparation of a series of standard solutions of copper for comparison and there is a question as to the permanency of these standards.

With the development of photoelectric colorimeters it is now possible to dispense with the use of standard solutions. About 2 years ago such an instrument called the photelometer was devised by Sanford, Sheard, and Osterberg (*7*) and recently similar instruments have been described by Eimer and Amend (*1*), by Yoe and Crumpler (*9*), by Zinzadze (*10*), and by Müller (*6*). In using them the intensity of light transmitted by a colored solution is correlated with the concentration of the constituent responsible for the color. It is necessary to use a suitable light filter in order to provide light of the proper wave length.

The spectrophotometric method for copper depends upon the fact that the percentage transmittancy of light of a given wave length for an ammoniacal copper solution is a function of the copper concentration. It is possible to construct a reference curve by plotting percentage transmittancy at a given wave length of a series of standard solutions of ammoniacal copper sulfate against the known copper concentrations and then by use of this curve to convert the percentage transmittancy of an unknown ammoniacal copper solution into concentration of copper. A similar procedure was followed by the writer in determining manganese in steel (*4*). Once constructed, such a curve may readily be used permanently, but the labor involved in its construction is an objection to it.

Since Beer's law has been shown (*6, 9*) to hold for ammoniacal copper solutions up to concentrations of almost 1 gram of copper per liter, the concentration of copper in a given solution can be calculated from the fundamental Lambert-Beer equation

$$I = I_0 \times 10^{-elc}$$

in which I_0 represents the intensity of the incident light of given wave length which enters the solution, I the intensity remaining after its passage through the solution, l the length in centimeters of the solution, c the moles of absorbing substance per liter of solution, and e a constant which is a measure of the absorption due to a single molecule and is called the molecular extinction coefficient.

The above equation may also be written

$$\log\frac{I}{I_0} = -elc$$

or

$$\log \frac{I_0}{I} = elc$$

The ratio $\frac{I}{I_0}$ may be evaluated by dividing 100 by the percentage transmittancy of the solution as determined by a spectrophotometer. To establish the value of the constant e for a given wave length it is necessary to determine the percentage transmittancy of a solution of known copper concentration. Theoretically a single measurement would be sufficient, but practically it is far better to take the average of a series of careful measurements made on solutions of different concentrations of copper.

Determination of Molecular Extinction Coefficients

A series of copper solutions was made by accurately weighing from 0.1 to 0.2 gram of copper wire, the purity of which had been determined electrolytically, and dissolving each portion in 5 ml. of concentrated nitric acid. After the addition of 5 ml. of concentrated sulfuric acid, the solution was evaporated on a hot plate to dense white fumes, allowed to cool, and then was diluted with 25 ml. of water. When all the copper sulfate had been dissolved, 30 ml. of 15 N ammonium hydroxide were added and the deep blue solution was diluted with 3 N ammonium hydroxide to 500 ml. at 30° C. in a volumetric flask. Various aliquots of these solutions were in turn diluted with 3 N ammonium hydroxide to 100 ml. at 30° C.

All transmission measurements were made with the photoelectric spectrophotometer built for Purdue University by the General Electric Company. This is the same instrument that was used and described by Mellon and Kasline in their recent work on solutions of ferric chloride (*5*). Measurements were made by setting the wave-length scale, adjusting the three slits to give the desired width of spectral band at the given wave length, and reading the transmission on the photometer scale. Readings were taken at 570, 580, and 590 mμ and each one was checked within ±0.1 per cent. The photometer scale was checked before each series of measurements by means of Bureau of Standards glasses. All transmittancies were obtained by dividing the transmission for the solution by that for the solvent at the same wave length. The cell used had a length of 1.968 cm.

As Yoe and Crumpler (*9*) point out, ammonia solutions show an appreciable absorption in the visible region and it is therefore necessary to use in measuring the transmission of the solvent an ammonia solution of the same concentration as is present in the copper solution. This was done by adding dropwise to the copper solution in the cell after the transmission had been observed just enough 1 M solution of potassium cyanide to decolorize the solution.

The average values obtained for e are

570 mμ	49.76
580 mμ	52.99
590 mμ	55.55

Determination of Copper in Ores and Mattes

The method was tested by applying it to the determination of copper in ores and mattes in which the copper had previously been determined by the iodide method. After the copper had been put into solution and excess ammonium hydroxide had been added, the copper was separated from the silica and the hydroxides of iron and aluminum by filtration as was done by Heath (*2*) in his colorimetric determination.

Procedure. Accurately weigh from 0.2500 to 1 gram of sample, depending upon the copper content, and transfer to a casserole. Cover with a watch glass, add 10 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid, and warm on the hot plate until all action has ceased and solution has been effected. Let cool, slowly add 5 ml. of concentrated sulfuric acid, and carefully evaporate from the uncovered casserole, keeping in constant motion until dense white fumes are evolved. This fuming is most conveniently done by use of an electric evaporating cone placed directly above the casserole. In such case it is not necessary to keep the casserole in motion. Let cool, carefully add 25 ml. of water, and warm to dissolve the copper sulfate.

Add slowly to the cool solution 30 ml. of 15 N ammonium hydroxide, and filter into a 250-ml. volumetric flask. Wash the residue with 3 N ammonium hydroxide until the washings come through colorless. By means of a stream of water from the wash bottle rinse the residue back into the casserole, being careful not to damage the filter, and add just enough concentrated sulfuric acid to dissolve the iron and aluminum precipitate. Reprecipitate by adding 5 ml. of 15 N ammonium hydroxide, add torn up bits of filter paper to hasten filtration, and filter through the original paper, catching the filtrate in the volumetric flask. Transfer the precipitate to the filter and wash with 3 N ammonium hydroxide until the volume of the filtrate is almost 250 ml. Make up the filtrate to the mark with 3 N ammonium hydroxide at 30° C. and mix thoroughly.

By means of the spectrophotometer determine percentage transmission of this solution in a 2-cm. cell at 570, 580, and 590 mμ. Then to the solution in the cell add dropwise just enough 1 M potassium cyanide to remove the color and determine the percentage transmission of this solution at the above wave lengths. The former figure multiplied by 100 and divided by the latter gives the percentage transmittancy of the copper solution.

Using the value of e given above for the wave length in question, calculate the percentage of copper in each case and take the average as the percentage of copper in the sample.

Notes

1. Convenient weights of sample: for ores containing less than 5 per cent of copper, 1 gram; from 5 to 10 per cent of copper, 0.5 gram; more than 10 per cent of copper, 0.25 gram.
2. The method of double precipitation of the iron and aluminum is more accurate, more conveniently carried out, and much more rapid than the process of precipitating the copper by aluminum that is generally used in the iodide method.
3. According to Heath (*2*), results with samples containing from 25 to 35 per cent of iron and aluminum oxides showed never more than 0.04 per cent of copper in the residue on the paper after the second precipitation and sometimes no copper at all.
4. Fuming down with sulfuric acid removes any lead as lead sulfate.
5. If the type of spectrophotometer is used in which the light passes through separate cells of solution and solvent simultaneously, the solvent is prepared by adding to a second portion of the solution just enough potassium cyanide solution to remove all the blue color.
6. Nickel and cobalt must be absent, since both give soluble colored complex ions with excess ammonia.
7. Other wave lengths might be chosen, but the three selected consistently gave the best results.
8. The following example will illustrate the method of calculation. Weight of sample, 0.2517 gram; transmission of solution at 580 mμ, 52.1 per cent; transmission of solvent, 89.1 per cent; cell length, 1.968 cm. The Lambert-Beer formula solved for c gives

$$c = \frac{\log \frac{I_0}{I}}{el} \text{ moles per liter}$$

$$c = \frac{\log \frac{I_0}{I} \times 63.57}{el} \text{ gram of copper per liter}$$

or,

$$\text{Since } I = \frac{\text{Transmission of solution} \times 100}{\text{Transmission of solvent}} \text{ and } I_0 = 100$$

$$\log \frac{I_0}{I} = \log 100 - (\log \text{transmission of solution} + \log 100 - \log \text{transmission of solvent})$$

$$\log \frac{I_0}{I} = \text{log transmission of solvent} - \text{log transmission of solution}$$

$$\log \frac{I_0}{I} = \log 89.1 - \log 52.1$$

$$\log \frac{I_0}{I} = 1.9499 - 1.7168 = 0.2331$$

Therefore,

$$c = \frac{0.2331 \times 63.57}{52.99 \times 1.968} \text{ gram of copper per liter}$$

Since the solution of the sample was made up to 250 ml.

$$\text{per cent copper} = \frac{0.2331 \times 63.57 \times 100}{52.99 \times 1.968 \times 4 \times 0.2517} = 14.12$$

The calculation can be made very quickly.

Copper was determined in nine low-grade sulfide ores and two mattes by following the procedure as given above. The results are shown in Table I, which also includes as a check the figures obtained by using the iodide method as given by Mahin (*3*).

TABLE I. RESULTS OBTAINED BY SPECTROPHOTOMETRIC METHOD

Sample No.	Sample Nature	Copper by Iodide Method	Copper Obtained from Transmittancy at: 570 mμ	580 mμ	590 mμ	Average Copper Found	Difference
		%	%	%	%	%	%
1	Ore	7.27	7.33	7.27	7.24	7.28	+0.01
2	Ore	6.27	6.27	6.29	6.29	6.28	+0.01
3	Ore	5.37	5.37	5.42	5.43	5.41	+0.04
4	Ore	3.94	3.98	3.93	3.90	3.94	0.00
5	Ore	3.03	3.09	3.09	3.08	3.09	+0 06
6	Ore	8.56	8.55	8.52	8.44	8.50	−0.06
7	Ore	8.22	8.27	8.26	8.25	8.26	+0.04
8	Matte	14.09	14.16	14.12	14.07	14.12	+0.03
9	Ore	2.24	2.22	2.20	2.17	2.20	−0.04
10	Ore	4.34	4.30	4.29	4.27	4.29	−0.05
11	Matte	21.61	21.80	21.61	21.61	21.67	+0.06

The spectrophotometric method is capable of giving results for copper in ores and mattes which are within ±0.10 per cent of the values given by the iodide method and many are much closer than that. Results may be duplicated on the same sample with a precision of about ±0.05 per cent. The method, while applicable especially to low-grade copper ores, may be used for ores of high copper content by suitable dilution of the solution.

Summary

The spectrophotometric method for copper, which depends upon measuring by a spectrophotometer the transmittancy of light of a given wave length through an ammoniacal solution of copper, has these advantages over the regular colorimetric method: It does not require a series of color standards, eliminates entirely matching color shades by eye, and gives results which are more dependable.

Its advantage over the photoelectric colorimetric methods consists in not requiring the use of a light filter or color screen. It is much easier merely to set the wave-length scale of a spectrophotometer at the desired figure than it is to find a suitable light filter. The instrument, however, is an expensive one that is not universally available.

The spectrophotometric method gives just as good results for copper as the iodide method does and is more rapidly and more conveniently carried out.

Acknowledgments

The writer wishes to express his sincere appreciation to M. G. Mellon, Department of Chemistry, Purdue University, in whose laboratory this investigation was carried on, and to thank him for the use of the Purdue spectrophotometer and for his helpful criticism and suggestions. Thanks are also given to H. W. Swank, W. B. Fortune, and G. Dragt of Purdue for their aid in adjusting the spectrophotometer.

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Differences in the Lactic Acid Percentages in Butters

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WHEN unsalted butter is purchased for use in ice-cream manufacture, it is highly desirable from the standpoint of keeping quality to know whether the butter was made from sweet or sour cream. In many instances, the score is sufficiently indicative, but inquiries addressed to this bureau indicate that a test that eliminates the personal factor is needed.

The most obvious possibility of distinction would seem to be in the proportions of lactic acid, both free and combined, present in the butters. For practical use for this purpose, the lactic acid determination should be rapid, the proportions of lactic acid should not change during storage of the butter, and, either the values obtained should be highly accurate, or, in case a high degree of accuracy is not obtainable, the values for sweet-cream and sour-cream butters should be considerably different.

Even in the simpler methods of determination of lactic acid given in the literature, it is recommended that protein and carbohydrates be removed in a preliminary treatment of the sample, since in the presence of these substances too high values are obtained. The methods of removal are tedious and the proportional errors in the determinations on the prepared samples may be from 3 to 15 per cent of the quantity of the lactic acid being determined. It was decided, therefore, to use samples without preliminary treatment, on the assumption that the error due to protein and carbohydrate would be a fairly constant one. It was hoped, furthermore, that the proportional error would be insignificant in comparison with

the differences measured. The results fulfilled hopes in these two respects.

Method

The method of determination adopted is that of Friedemann, Cotonio, and Shaffer (*1*), which consists of oxidizing an acidified sample by means of an oxidation-reduction system composed essentially of divalent and quadrivalent manganese compounds. The oxidant is renewed by means of addition of potassium permanganate solution. Under these conditions, lactates and lactic acid are oxidized to acetaldehyde. The aldehyde is absorbed in sodium bisulfite solution and the quantity of bisulfite thus bound is determined by titration with standard iodine solution. When 0.01 *N* iodine solution is used for the titration, the butter sample should weigh 10, 20, or 30 grams, depending on the percentage of lactic acid present. The sample is weighed directly into the flask in which the oxidation is to take place and the oxidation is carried out without any preliminary treatment of the sample.

Determinations

Preliminary determinations were made on fourteen commercial samples of unknown history and two samples of known history. Nine of the samples gave percentages of apparent lactic acid ranging from 0.012, for a sample known to be sweet-cream butter, to 0.023; the other seven samples gave percentages from 0.117 to 0.217, a known "centralizer" butter giving 0.185. The remarkable feature is that there were no butters giving values between 0.025 and 0.100 per cent. It is of passing interest that the titratable acidity of the low lactate butters was of the order of 0.08 per cent, and that of the high lactate butters was of the order of 0.16 per cent, these consistencies indicating, apparently, that none of these butters was from partially neutralized cream.

Forty samples of butter were then prepared from two lots of cream, each lot being subdivided and given various treatments before and after churning. Typical analytical results on these butters are given in Table I. All samples of butter were washed and worked in the customary way, unless it is otherwise stated.

Table I. Apparent Lactic Acid in Butters of Known History

History	Apparent Lactic Acid
	%
0.15[a] per cent acid in cream, butter unwashed	0.025
Same, butter washed and worked	0.015
Whey butter	0.017
0.23 per cent acid in cream	0.024
Same, starter added to butter in churn	0.038
0.30 per cent acid, mixture of raw and pasteurized	0.023
Same, butter worked with limewater	0.021
Same, worked further with limewater	0.016
0.26 per cent acid, reduced to 0.18 per cent by water	0.013
0.35 per cent acid, reduced to 0.25 per cent by skim milk, butter unwashed	0.099
Same, butter washed	0.027
Same, butter washed with $NaHCO_3$ solution	0.018
0.38 per cent acid	0.142
0.40 per cent acid, reduced to 0.22 per cent by water	0.058
0.42 per cent acid, neutralized to 0.14 per cent, butter unwashed	0.085
Same, butter washed	0.055
Same, butter washed with $NaHCO_3$ solution	0.033
0.45 per cent acid, neutralized to 0.05 per cent by limewater	0.061
0.80 per cent acid, moldy, bitter; butter unwashed	0.245
Same, butter washed	0.262
Same, butter washed with $NaHCO_3$ solution	0.110
0.80 per cent acid, neutralized to alkaline side, unwashed	0.099
Same, butter washed	0.038

[a] These values are in all cases titratable acidities.

In Table II are results obtained from twenty samples of butter made commercially in the South in several different creameries. All except four of these samples were made from partially neutralized cream. The sweet-cream butters show consistently less than 0.025 per cent of apparent lactic acid; the partially neutralized samples, consistently more than 0.050 per cent.

Table II. Apparent Lactic Acid in Samples of Commercial Butter

Sample	Titratable Acidity of Cream: Before neutralization	Titratable Acidity of Cream: When churned	Apparent Lactic Acid in Butter
	%	%	%
1-R	0.55	0.28	0.063
2-R	0.80	0.15	0.051
3-R	0.60	0.25	0.059
4-R	0.70	0.24	0.075
5-R	0.80	0.22	0.071
1-N	0.65	0.25	0.068
2-N	0.60	0.23	0.067
3-N	0.65	0.24	0.084
4-N	0.82	0.24	0.074
5-N	0.73	0.23	0.061
1-K	0.78	0.23	0.057
2-K	0.56	0.25	0.062
3-K	0.72	0.28	0.057
35-B	0.16	0.16	0.023
37-B	0.14	0.14	0.011
38-B	0.14	0.14	0.020
39-B	0.16	0.16	0.021
40-M	0.84	0.27	0.082
41-M	0.84	0.27	0.081
43	1.30	0.24	0.127

Table III. Effect of Storage at 15° C. on Percentage of Lactic Acid in Butter

Date	Apparent Lactic Acid
	%
April 2, 1934	0.018
June 15, 1934	0.017
May 5, 1934	0.018
June 14, 1934	0.018
April 2, 1934	0.047
June 14, 1934	0.052
April 28, 1934	0.071
June 14, 1934(moldy)	0.066
March 26, 1934	0.217
June 15, 1934(moldy)	0.226

Table III gives results of determinations on five samples before and after storage at 15° C. (60° F.). The authors have also analyzed samples of butter that had been in commercial storage for as long as 9 months and found less than 0.025 per cent of apparent lactic acid, this showing that sweet-cream butter, even on long storage, does not develop lactic acid in appreciable quantity.

Conclusions

Detailed discussion of the results seems unnecessary. Study of the tables will bring out several points not mentioned here, but the most important conclusions appear to be as follows:

1. Butter made without the use of starters from normal cream containing less than 0.25 per cent of titratable acid will contain less than 0.025 per cent of apparent lactic acid.
2. Butter made without the use of neutralizing agents from normal sour cream containing more than 0.40 per cent of titratable acid will contain more than 0.100 per cent of apparent lactic acid.
3. Butter made from sour cream neutralized to approximately 0.20 per cent titratable acidity will contain more than 0.050 per cent of apparent lactic acid.
4. Dilution of the cream with water or sweet skim milk, or washing of the butter with alkaline water, will somewhat decrease the percentage of apparent lactic acid in the butter. Such procedures are, however, not likely to be encountered commercially, since they injure the flavor and texture of the butter.
5. Storage of butter even at temperatures considerably higher than those customarily used for butter storage has no effect on the percentage of apparent lactic acid present.

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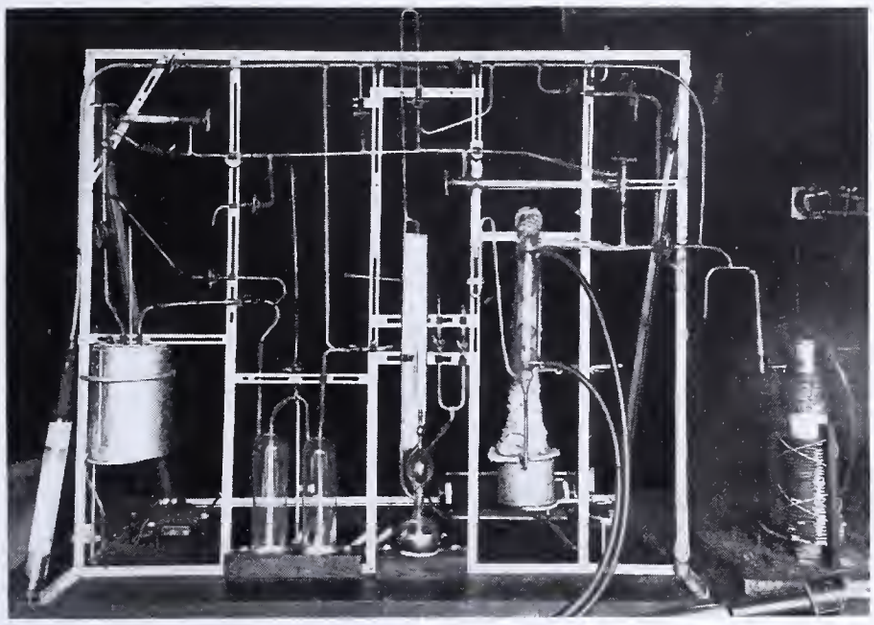

FIGURE 1. PHOTOGRAPH OF ASSEMBLED APPARATUS

Determination of Oxygen and Nitrogen in Steel

Improvements in the Vacuum-Fusion Method

JOHN CHIPMAN[1] AND M. G. FONTANA,[2] University of Michigan, Ann Arbor, Mich.

THE development of reliable methods for the determination of the gaseous elements in steel has done much to clarify our understanding of their occurrence and effects, and has played an important part in recent advances in steel-making practice based upon the control of ferrous oxide in the liquid steel. The vacuum-fusion or hot-extraction method, which was developed by Jordan (*6, 7, 15*) and his associates at the Bureau of Standards and by the late Professor Oberhoffer (*8, 9, 10, 14, 16*) and his students at Aachen, is to be regarded as the most dependable method for the determination of total oxygen and total nitrogen in ferrous metals. This paper describes the apparatus and technic employed in the Department of Engineering Research at the University of Michigan and introduces several changes which were designed to enhance the simplicity and speed of the determination, as well as to improve its accuracy for steels of low oxygen content.

Principle of the Method

At sufficiently high temperatures and low pressures all oxides are reduced by carbon, forming carbon monoxide. A graphite crucible is heated in vacuum to remove adsorbed gases. The steel sample is then melted in the crucible, its oxides are reduced to carbon monoxide, its nitrides and hydrides are decomposed, and any adsorbed or dissolved gases are liberated. The gases are pumped out continuously and are collected and analyzed. In order to effect the reduction of all the oxides that are found in steel, including alumina, it has been found necessary to employ temperatures above 1550° C. This is most easily accomplished by high-frequency induction heating, a method first applied by Jordan, by means of which the crucible may readily be heated to 1900° C. without endangering the silica furnace tube.

Limitation of Method and Sources of Error

The chief failing of the vacuum-fusion method is that as ordinarily employed it yields only total oxygen and total nitrogen and gives no information as to the form of combination of these elements in the sample. A fractional method has recently been suggested by Reeve (*11*) in which the gases evolved at four different temperatures are assumed to represent the four principal oxides in steels. While this modification has been very useful in the study of weld metal, it will doubtless require special development for each type of material to which it is applied.

The most important source of error is that due to the presence of metallic vapors in the furnace during the evolution of gases from the metal. These vapors condense as a metal film on the colder parts of the furnace and tend to reabsorb the gases. Manganese and aluminum are the two most volatile metals found in steels and both lead to "metal film" interference.

All the investigators of the method recognize this volatile metal interference, but there is some disagreement as to its seriousness. Von Seth (*12*), on one extreme, regards the manganese interference as an insuperable obstacle, whereas Bardenheuer (*1*) claims successful operation with manganese contents up to 1 per cent. Diergarten (*2, 3, 4*) states that the oxygen determination will be inaccurate if the material in the graphite crucible contains over 0.7 per cent manganese or 0.3 per cent aluminum. Vacher and Jordan (*15*) found that over 0.2 per cent manganese will interfere if several analyses are carried out successively in the same graphite crucible. The metal film error can be avoided by providing a high speed removal of the evolved gases, by avoiding the

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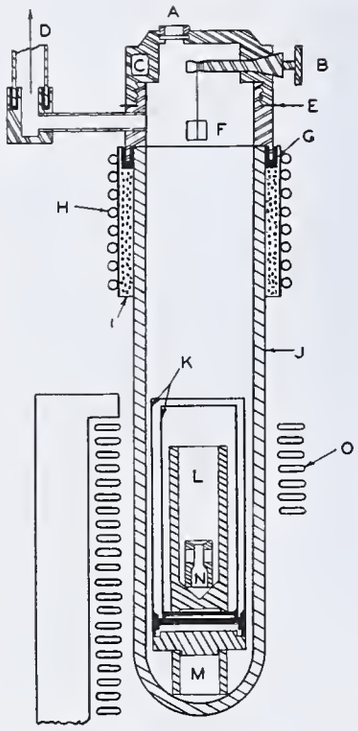

FIGURE 2. SECTION OF VACUUM-FUSION FURNACE

re-use of a crucible in which a sample containing high manganese or aluminum has been analyzed, and by cleaning the furnace tube after each such analysis.

There has been some uncertainty concerning the completeness of reduction of all the oxides present in the steel, especially the oxide of aluminum. There can be no doubt as to the complete reduction of the oxides of iron and manganese. Vacher and Jordan have shown that the silicates and silica as they ordinarily exist in steels are completely reduced. Attempts to show conclusively whether or not alumina is completely reduced have led to some contradictory reports. This uncertainty has been partially clarified by Ziegler's (*17*) work in which he showed that when powdered alumina is packed into a hole in a steel specimen it is not reduced in vacuum fusion even at 1700° C. On the other hand, when powdered graphite is mixed with the alumina and the mixture is analyzed in the same manner, the oxygen of the alumina is recovered. The effect of the graphite is merely to prevent lumping of the alumina. Further evidence that oxygen of the alumina in steel is determined by this method will be described in a later section of this paper.

Since it is virtually impossible to remove the last traces of gases from even the purest commercial graphite, it is necessary to apply a blank correction because of the continuous evolution of gas from the crucible. Obviously, the lower the gas content of the steel, the more important it is to reduce the blank correction to a minimum. Considerable work has been done in this laboratory on the deoxidation of steel and on the melting and refining of Chromel, an alloy of extremely low oxygen content. This necessitated the development of a technic by which the blank could be reduced to about one-fifth or one-tenth of its usual amount.

Description of Apparatus

Figure 1 is a photograph of the assembled apparatus showing, from right to left, the induction furnace in which the specimen is melted, the vacuum pump, McLeod gage, and analytical system.

FURNACE. Figure 2 shows a section of the assembled furnace. The silica tube, *J*, is 30 cm. (12 inches) long by 6.8 cm. (2.625 inches) outside diameter. The graphite crucible, surrounded by the concentric radiation shields, *K*, is located at about the center of the field of the induction coil, *O*. The specimen, *F*, is suspended by fine nickel wire (36 B and S gage, 0.13 mm.) from the stainless steel windlass, *B*, which is ground into the brass head and lubricated by vacuum grease. The head is made of annealed, cold-rolled brass. Its upper portion is water-cooled and has a small Pyrex glass window, *A*, held down by a threaded brass ring and rubber washers. The two parts of the head are threaded together and made vacuum-tight by an ordinary mason jar ring, *E*. The lower part is cemented to the silica tube by picein wax held in the groove, *G*, which is formed by the outer brass ring and water cooled by the copper coil, *H*. The lower part of the head contains the outlet to the vacuum pump which is attached to the glass tubing, *D*, by an easily made picein seal. Duplicates of the lower part were made, so that each silica tube in use could be equipped with one, and the seal at *G* having once been made need never be broken. This simple and easily removable head construction permitted a quick exchange of tubes or crucibles and greatly facilitated the task of cleaning the tube.

A feature of the furnace which has been especially helpful in reducing the blank correction and increasing the operating temperature is the method of supporting the crucible and of protecting the outer tube from its intense radiation.

A photograph of the crucible, *L*, the two graphite shields, *K*, and the plug, *N*, is shown as Figure 3. These were all made from Acheson graphite. The shields were turned out from a solid 5-cm. (2-inch) electrode and have a wall thickness of 0.8 mm. (0.03 inch). The walls were slotted to prevent heating due to induced currents. The bottoms of the shields and crucible were recessed to diminish thermal contact with the base. The shoulders on the insides of the shields insured proper spacing.

The purpose of the shields is to protect the walls of the furnace from excessive heating by radiation. They not only accomplished this in excellent fashion, but also eliminated an important source of trouble that was encountered when refractory shields were used—namely, the evolution of gases that occurred when the hot crucible touched the refractory shield. The outer graphite shield stayed cold enough so that no appreciable disturbance appeared if the whole internal assembly tilted slightly and touched the silica walls of the furnace. The graphite shields also permitted rapid heating, and consequently rapid degassing, of the crucible because they were immune from cracking due to large temperature gradients, which was a very disturbing factor when porcelain or sillimanite protectors were used. These graphite shields, in addition to being fairly easy to make, possessed remarkable strength and failed only when subjected to severe mechanical shock. This shield arrangement made possible the heating of the crucible to 1900° C. without danger of the quartz tube crushing or becoming permeable.

The crucible was made by drilling a 22-mm. (0.875-inch) hole in a 32-mm. (1.25-inch) rod. The bottom was slotted to prevent overheating of the lower portion of the crucible. The purpose of the plug, *N*, is to prevent spattering of the molten metal during gas evolution. When the sample, resting on top of the plug after lowering, begins to melt, it slips down through the hole in the plug and is thus effectively covered before any appreciable amount of gas is given off. The bubbles of gas formed through reduction by the carbon are broken up and the loss due to spattering is minimized. The plug also increases the area of contact between carbon and molten metal, thus favoring more rapid reduction. The use of this arrangement was imperative in the analysis of metals of high gas content, wherein large globules of metal would have otherwise been completely ejected out of the crucible because of the violent ebullition of gas. On the other hand, it was found that when the sample contained large amounts of alumina the use of the plug was detrimental to its complete reduction. This point will be explained later.

FIGURE 3. PHOTOGRAPH OF CRUCIBLE, GRAPHITE SHIELDS, AND PLUG

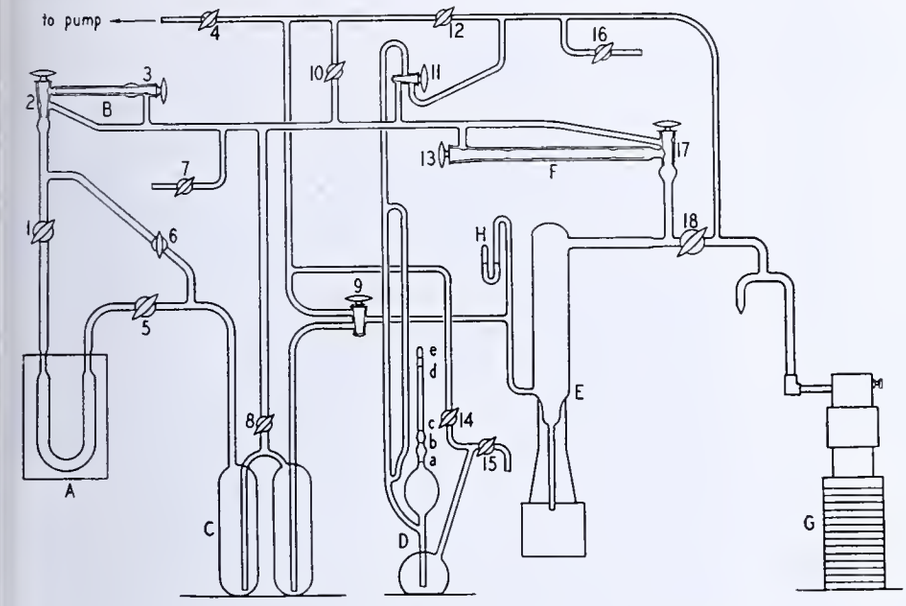

FIGURE 4. DIAGRAM OF ANALYTICAL APPARATUS

The graphite assembly rests on a magnesia base and a magnesia ring, *M*, both made by tamping powdered fused magnesia into a graphite mold and firing by induction in the neighborhood of 2000° C. The reaction at the point of contact of the graphite shield and magnesia base is practically nil because of the small area in contact and the comparatively low temperature of the shield. This was an important factor in reducing the blank correction.

ANALYTICAL TRAIN. The storage and analysis train are supported by a framework of 1.9-cm. (0.75-inch) angle iron resting on a heavy wooden base. Figure 4 is a sketch of the whole apparatus drawn approximately to scale.

The two-stage mercury diffusion pump, *E*, removes the gases evolved from the sample and stores them at low pressure in the reservoirs, *C*. After gas evolution has ceased, the same pump acts as a circulating mechanism to draw the gas through the copper oxide furnace, *A* (at about 340° C.) and through the absorption tubes, *B* and *F*. The tube to the left of stopcock 4 connects to a Cenco "hivac" or preferably the larger "megavac" oil pump. The mercury pump operates very efficiently against back pressures up to 12 mm.

The absorption tubes, *B* and *F*, are of an entirely new design. Previous experience with tubes which could be removed and weighed showed that the gravimetric determination was inferior in speed and accuracy to the volumetric. The removable feature was therefore eliminated, with the result of simplifying the construction and speeding up the circulation and absorption of gases. Tube *B* contains loosely packed phosphorus pentoxide, held in place by two wads of cotton, for removing water vapor from the system. This tube is efficient as long as there is any dry powder remaining in it.

Tube *F*, containing ascarite for absorbing carbon dioxide, is shown in better detail in Figure 5. The inner plug which forms the stopcock and holds the absorbing agent is easily removable and is made in duplicate so that the spent plug may be removed and a freshly loaded plug quickly inserted. The volume between the two constrictions is filled with ascarite, while that to the right of the right constriction is filled with phosphorus pentoxide, the two absorbents being held in position by wads of cotton. Before loading into the absorption tube, the ascarite is vacuum-desiccated over phosphorus pentoxide. One tube of ascarite is usually sufficient for about 15 analyses of steel of normal gas content.

The McLeod gage, *D*, is a specially constructed multistage instrument carefully calibrated by mercury weighings. It is read by observing the height in the open arm when the mercury in the closed arm is brought to one of the designated points shown by letters in Figure 4. The factors by which the observed height must be divided to give the pressure are: *a*, 23.5; *b*, 120.2; *c*, 552; *d*, 2760; *e*, 5520.

CALIBRATION. The storage system into which the gases are pumped during extraction consists of the exhaust side of the mercury pump, the two bulbs, *C*, the copper oxide furnace, the McLeod gage, and the connecting tubing. The volume of the storage system was determined with and without the absorption tubes open.

A known volume of purified nitrogen was admitted from a calibrated buret, which consisted of 8-mm. Pyrex tubing mounted on a meter stick and calibrated over its entire length by mercury weighings. The pressure before and after admission of the nitrogen was read with the McLeod gage. From these two pressures and the volume of gas admitted, the volume of the storage system was readily calculated. The total volume of the storage system, including the two absorption tubes, is 1810 cc. This was calculated to millimoles of gas per millimeter of pressure and expressed as a function of room temperature as in Figure 7.

Procedure

PREPARATION OF SAMPLE. The sample to be used for a determination should be as representative of the metal to be analyzed as possible. For example, a "pie slice" is usually taken from circular ingots or test bars. Whenever possible, a complete cross section is most desirable. The sample is first ground on an emery wheel to remove all surface scale, next pickled in alcohol and hydrochloric acid, and then washed first in alcohol and then in ether.

The weight of the sample should be chosen so as not to yield too much gas for the mercury pump to handle or too small an amount of gas to be accurately analyzed. In case considerably more gas is evolved than expected, some of the gas may be removed, after reading the total storage pressure, by the oil fore pump and only the remainder of it analyzed. This procedure prevents the too rapid exhaustion of the ascarite.

If the samples do not contain too much aluminum or manganese, two or three of them may be strung up in the furnace at the same time. When they are lowered, the first one in line drops off into the crucible when the nickel wire holding it melts and the others are then quickly raised and held in the upper part of the furnace until the first sample has been

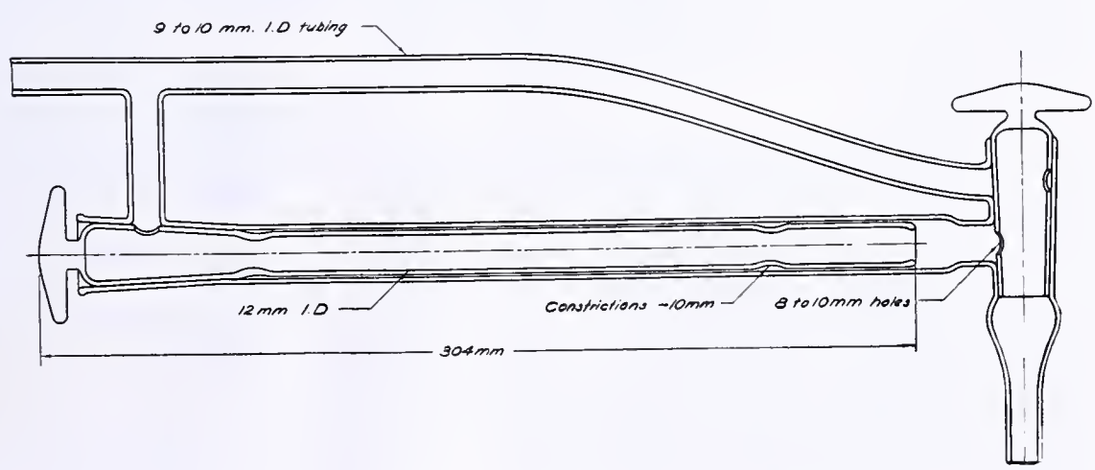

FIGURE 5. ABSORPTION TUBE FOR VACUUM-FUSION APPARATUS

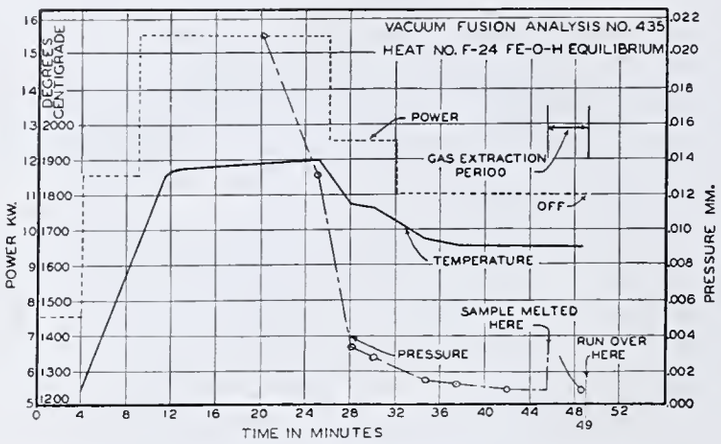

Figure 6. Performance Curves for Vacuum Furnace

completely analyzed. This procedure permits the analysis of two or three specimens without opening the furnace to the atmosphere.

Preparation of Analytical System. Except for the glass tubing between cock 9 and the mercury pump, all the storage system is thoroughly evacuated by the diffusion pump before any gases are pumped into it. The absorbents may be shaken up by turning the inner plugs of the absorption tubes (cocks 3 and 13). Air is occasionally admitted into the copper oxide furnace to oxidize any reduced copper that may be present. After air has been admitted into the storage system, the glass tubing is gently flamed under high vacuum with a Bunsen burner. The only important difficulty encountered in operating the analytical system has been in obtaining a satisfactory lubricant for the stopcocks. Formerly, it was possible to obtain a fairly good product by melting together the greases obtained from two supply houses. Unfortunately, one of these suppliers "improved" his product and now it is necessary to prepare one's own vacuum grease by the tedious method of Shepherd and Ledig (*13*).

Furnace Preparation. Figure 6 shows performance curves which give a graphic account of what occurs in the vacuum furnace from the time the power is turned on to the end of the gas extraction. In this particular analysis, a new graphite crucible was used and was degasified at a maximum temperature of 1900° C. and a converter setting of 15.5 kw. The preliminary heating time for any subsequent runs in a used crucible would be much shorter and at a converter setting of only about 12.5 kw. The first stages of the degasifying period are carried out under an oil pump vacuum. In the run illustrated, the diffusion pump was turned on to the furnace at the 18-minute mark or 2 minutes before the first pressure reading was taken. Prior to this the diffusion pump had been used to evacuate the storage system. The temperature is read by means of a disappearing filament-type optical pyrometer which is sighted through the prism shown in Figure 1. The pyrometer was calibrated using this prism and a similar sight glass.

Extraction of Gases. When the temperature of the crucible has been adjusted at about 1650° C., and after the pressure in the furnace has dropped to 0.001 mm. or less, the sample is lowered into the crucible and melted. The furnace pressures vary from e-2 to e-5 readings on the McLeod gage, which correspond to approximately 0.0004 to 0.0001 mm., respectively. After the sample has melted, pressure readings are taken on the furnace until the pressure drops to what it was before the sample was lowered and then the furnace cock is closed and the power shut off. In the analysis shown, the extraction time was only about 4 minutes because the oxygen was all present as easily reducible ferrous oxide. In commercial steels, especially the aluminum-killed ones, complete extraction sometimes requires 25 minutes because of the presence of more stable oxides.

Analysis of Gases. The gases from the furnace are all pumped into the storage system where they are analyzed. The mercury pump is used to circulate the gases through the copper oxide furnace and the absorption tubes. The water vapor formed is absorbed by the phosphorus pentoxide and the carbon dioxide by the ascarite. The pressure drop after each absorption is recorded and the amounts of gases absorbed can be calculated from these pressure drops and the known volume of the system. The curves showing the millimoles of gas present per millimeter pressure in the storage system at room temperatures are shown in Figure 7. Before the gases are circulated for absorption, the McLeod gage is evacuated in order to eliminate the "dead portion" of the circulation system which would be present if this were not done.

Blank Corrections. In order to establish the amount of the blank correction, a number of runs were made in which no sample was added, the gases collected being those evolved from the crucible itself. At the same time the rate of increase of base pressure in the storage system was determined at furnace pressures ranging from e-3 (0.0005 mm.) to e-8 (0.0015 mm.). In practice, the time used in computing the blank was the sum of the time that would have been required to accumulate the measured base pressure plus the elapsed time from measurement of base pressure to the end of the extraction. The time correction and the total blank are

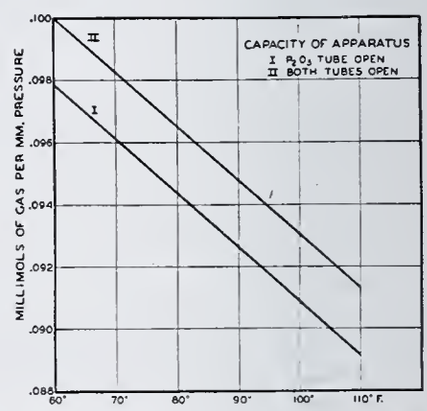

Figure 7. Volume of Apparatus Expressed in Millimoles per Millimeter

shown in Figures 8 and 9. It has been remarked elsewhere that a prerequisite of accuracy is a small blank. Virtually all the authors' runs have had a total blank correction of less than 0.01 millimole. The gases constituting the blank were found to analyze, on the average, 60 per cent carbon monoxide, 25 per cent hydrogen, and 15 per cent nitrogen.

Discussion and Results

Speed, Precision, and Accuracy of Apparatus. The time required for a complete analysis by the vacuum-fusion method has been considerably shortened. A study of the performance curves in Figure 6 will indicate clearly the length of time required for the preparation of the furnace and the degasification of the sample. A new crucible was used in this run. The mean time required for the gas extraction is about 15 minutes, although 25 minutes has been required in some cases. Forty minutes for the bake-out, 5 to 15 minutes for gas extraction, 5 minutes to remove moisture, 10 minutes to oxidize hydrogen and absorb water vapor, and 15 minutes for carbon dioxide removal, represent good averages. The length of time, therefore, required for an analysis is from 75 to 85 minutes, depending on the type of steel or metal analyzed. A second run in a crucible requires a shorter bake-out

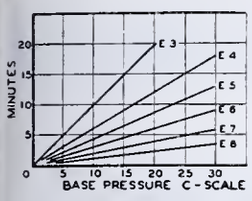

FIGURE 8. TIME CORRECTION FOR BASE PRESSURE

Time to be added to blank to compensate for base pressure in system.

period. Replacing the furnace is only a matter of minutes and the preparation of the next sample, or samples, can be accomplished during the absorption period. The storage system may be prepared during the time required to change furnaces and during that part of the bake-out period when the furnace is only under oil pump vacuum.

The precision and accuracy of the vacuum-fusion method have been greatly increased in this apparatus. For samples of not unusual gas contents, the oxygen and nitrogen can be readily determined with a precision of 0.001 per cent and a probable accuracy of ±0.002 per cent. The hydrogen determination is not very reliable and duplicate analyses often differ by as much as 0.0005 per cent. The reproducibility of the oxygen and nitrogen analyses by different operators is well illustrated in Table I. Note the two-hundred fold range of oxygen content covered with precision.

TABLE I. REPRODUCIBILITY OF ANALYSES

Sample	Date of Run	Sample	O	N	Operator
		Grams	%	%	
SMA-15	11-2-33	25.7	0.0011	0.0051	Fontana
SMA-15	12-5-33	48.0	0.0013	0.0052	Chipman
BS 7	8-19-34	9.3	0.110	0.0045	Fontana
BS 7	10-26-34	11.0	0.109	0.0044	Raynor
F 70	8-7-34	2.97	0.210	nil	Fontana
F 70	8-8-34	5.23	0.208	nil	Fontana

REDUCTION OF ALUMINA. In attempting to answer the question of the recovery of oxygen from the alumina in steel, it seemed best to employ steel samples containing large quantities of this oxide formed by reaction in the liquid steel. A method for determining oxygen in liquid steel was introduced by Herty (*5*) and has come into fairly general use. A spoonful of liquid steel is deoxidized by aluminum, cast into a mold, and analyzed for Al_2O_3 by solution of the metal in nitric acid. Samples secured by an improved form of this method from several heats of mild steel low in carbon, manganese, and impurities were analyzed for alumina and for oxygen. The results are given in Table II and show a recovery of 80 to 100 per cent of the oxygen by vacuum fusion. Duplicate samples are grouped together in brackets.

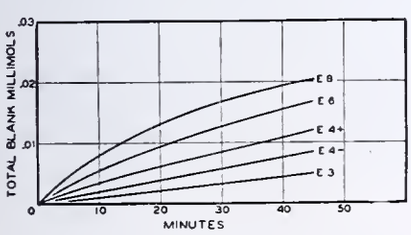

FIGURE 9. BLANK AS A FUNCTION OF TIME AND FURNACE PRESSURE

One cause of low results in these specimens was found in the tendency of the metal to melt away from the alumina leaving part of it as a dry powder adhering to the crucible wall. This error was increased by the presence of the plug in the crucible and was minimized by lowering the specimen into the molten residue from a previous analysis. Since the alumina content of any ordinary steel is of a lower order of magnitude than that of these specimens, it is altogether unlikely that incomplete reduction of alumina would ever constitute a serious source of error.

Summary

Improvements in technic and changes in construction have resulted in a vacuum-fusion apparatus that yields reliable results for the determination of oxygen and nitrogen in metals, chiefly in iron and steel. Except for very special cases, all the obstacles in the path of the successful operation of the method have been overcome. The accuracy of the method has been increased and the length of time required for a determination has been considerably shortened. It has been shown that the oxygen content of alumina formed in the deoxidation of liquid steel by aluminum is recovered by this method. Over six hundred successful vacuum-fusion analyses on a wide variety of steels, cast irons, and nonferrous materials have been completed in this laboratory.

TABLE II. ANALYSES OF ALUMINUM-KILLED SPECIMENS

No.	Oxygen by Al_2O_3	Oxygen Vacuum-Fusion
1	0.057	0.052
2	0.058	0.050
3	0.066	0.056
4	0.068	0.060
5	0.059	0.050 0.059
6	0.050	0.039 0.042
7	0.049	0.042
8	0.040	0.045

Acknowledgments

The writers gratefully acknowledge their indebtedness to D. W. Murphy for aid in setting up and standardizing the apparatus; to H. Hamner of the Union Carbide and Carbon Research Laboratories for suggesting graphite shields; and to C. W. Raynor for a number of analyses, including those on the aluminum-killed samples. The difficult glass parts were made by G. Kessler. Thanks are also extended to F. G. Norris and O. B. Ellis of the American Rolling Mill Company for sampling and analysis of the aluminum-killed samples.

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RECEIVED July 11, 1935

A. S. T. M. Activities in Ferrous Metals

The Steel Committee has under way the development of new specifications and revisions in some existing standards. Requirements for fabricated reinforcement material, wire mesh, wire mats, etc., are being developed and separate specifications for steel castings for marine use are under consideration. The committee has decided to standardize requirements for 4 to 6 per cent chromium steel still tubes and heat-exchanger and condenser tubes. In the high-temperature field a draft of requirements for nut material for use in bolting for high-temperature or high-pressure service has been circulated in the committee and action will be taken thereon during the year. Progress has been made in the study on specifications for high-strength structural rivets and revisions in the existing standard specifications for structural nickel steel (A8–29) are under way.

Colorimetric Determination

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University of Wisconsin, Madison, Wis.

IT HAS long been known and appreciated that the thiocyanate–stannous chloride method for molybdenum yields concordant results only when standard and sample are treated in exactly the same manner. The similarity of the reaction to the Geilmann reaction of rhenium and the profound effect which slight changes in concentrations of reagents have upon the rhenium color (*1*) led the authors to believe that a study of the actual effect of the variables involved might yield results of value to the analyst.

The Eastman universal colorimeter (*3, 4*) was used to follow all color changes. As in the case of rhenium, it was found that the color could be duplicated in the field by means of the blue wedge, provided slight corrections were made with the other wedges.

A stannous chloride solution was prepared from reagent quality salt, standardized, and adjusted so that it contained 2.0 per cent of $SnCl_2$. The hydrochloric acid content of the solution was 2.3 per cent. A 10.0 per cent potassium thiocyanate solution was prepared from the recrystallized salt. The hydrochloric acid solution was prepared by diluting constant-boiling acid with water. Pure molybdic acid was converted to the sodium salt with a minimum amount of sodium hydroxide and dissolved in water to yield a solution containing 10γ per ml. The method followed was first to add to the colorimeter tube the desired amount of molybdenum and then follow this with a mixture of hydrochloric acid, stannous chloride, potassium thiocyanate, and water. The final volume in every case was 50 ml. The time at which the reagents were added to the molybdenum was taken as zero. Colorimeter recordings were made at intervals, the magnitude of which was determined by the rate of color change.

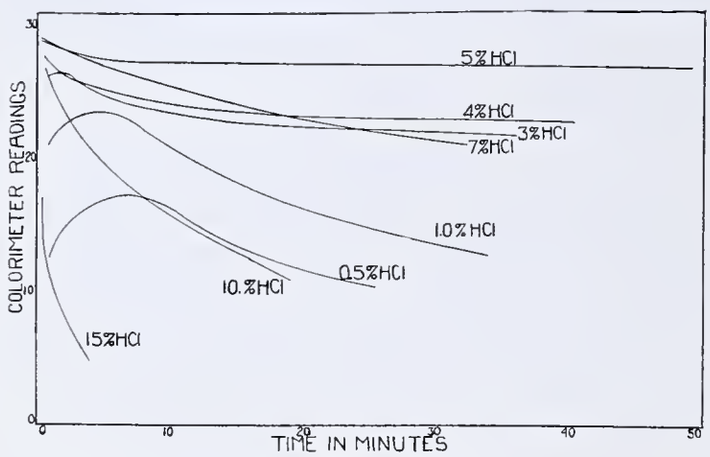

FIGURE 1

Figure 1 illustrates the effect of various hydrochloric acid concentrations upon the color developed in a solution containing 100γ of molybdenum, 1.0 per cent of potassium thiocyanate, and 0.80 per cent of stannous chloride. When the hydrochloric acid concentration was low—i. e., 0.5 per cent—the color reached a maximum at the end of 8 minutes and faded to less than its initial value at the end of 25 minutes. As the concentration increased, the maximum shifted toward zero time and less fading was evident until a concentration of 5 per cent was exceeded. In higher concentrations of acid the fading was marked.

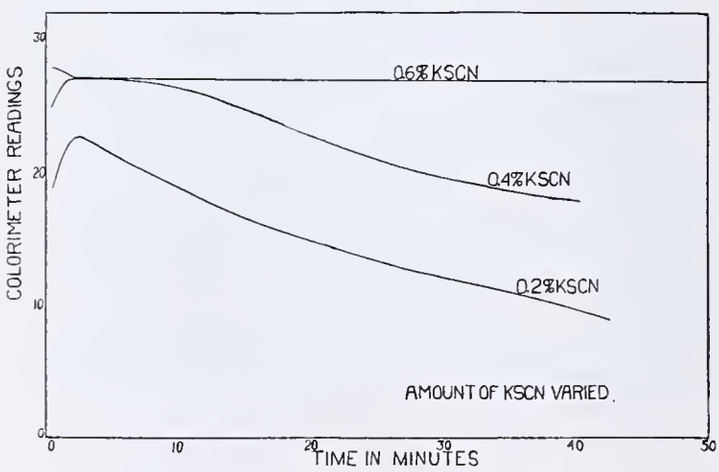

FIGURE 2

The effect of varying the potassium thiocyanate concentration is shown in Figure 2. The colors were developed in 5.0 per cent of hydrochloric acid and 0.8 per cent of stannous chloride. In solutions containing less than 0.6 per cent of potassium thiocyanate the fading was marked. Above this value there was little or no change produced.

The molybdenum thiocyanate reaction, unlike the Geilmann reaction, is not particularly sensitive to fluctuations in

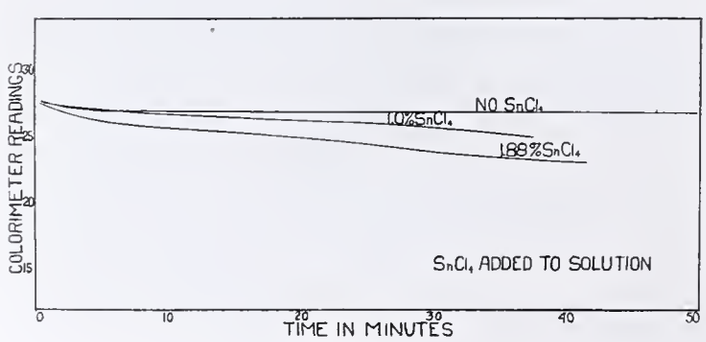

FIGURE 3

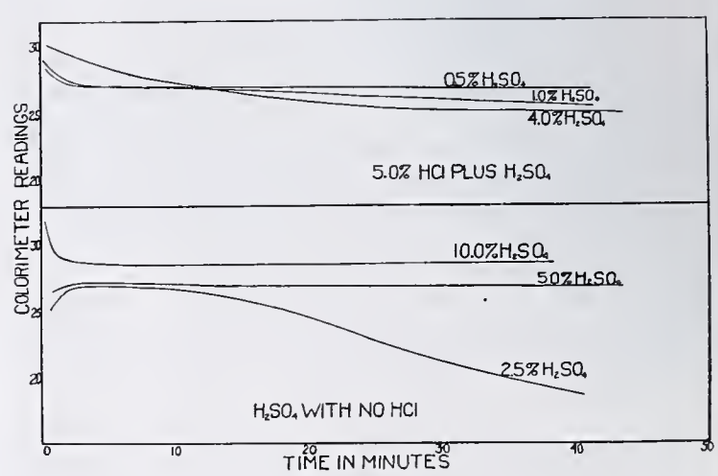

FIGURE 4

# of Molybdenum

A Study of Variables Involved

stannous chloride concentration. With 100γ of molybdenum it was found that a 0.04 per cent concentration produced a color concentration equal to that of a twenty-fold excess. No great differences were detected in either the speed of development or the rate of fading. In actual practice the determination is usually carried out in the presence of large amounts of ferric iron, which is reduced by the stannous ion with the production of stannic chloride. The effect of stannic chloride, as is to be seen in Figure 3, was to promote a slight fading of the color. After the first few minutes the effect was not marked even in concentrations as high as 1.88 per cent. Sulfuric acid in low amounts caused a rapid initial decrease, whereas higher concentrations contributed to fading (Figure 4). In the absence of hydrochloric acid (except for 0.46 per cent added with the stannous chloride) maximum color was not reached below 10 per cent of sulfuric acid and at this concentration initial fading was rapid. In 5 per cent solution the color was unusually stable.

Nonaqueous Extractors

The effect of saturating petroleum ether–ethyl ether (*5*) mixtures by shaking the solvent with the reagents before extraction is shown in Figure 5. The curves were constructed from observations made upon 35 per cent petroleum–65 per cent ethyl ether solutions containing 100γ of molybdenum. The initial intensities were about the same and both passed through minima at the end of 1 hour, after which the change was too gradual to be of great consequence.

Cyclohexanol (*2*) when saturated with the reagents exhibited practically no fading over a period of a few hours (Figure 6), but on long standing the color slowly became deeper (Figure 7). It is interesting to note that the color produced by a given amount of molybdenum is more intense when dissolved in cyclohexanol than in ether. Cyclohexanol is, however, difficult to handle, separates slowly from aqueous solutions, and sometimes develops a turbidity.

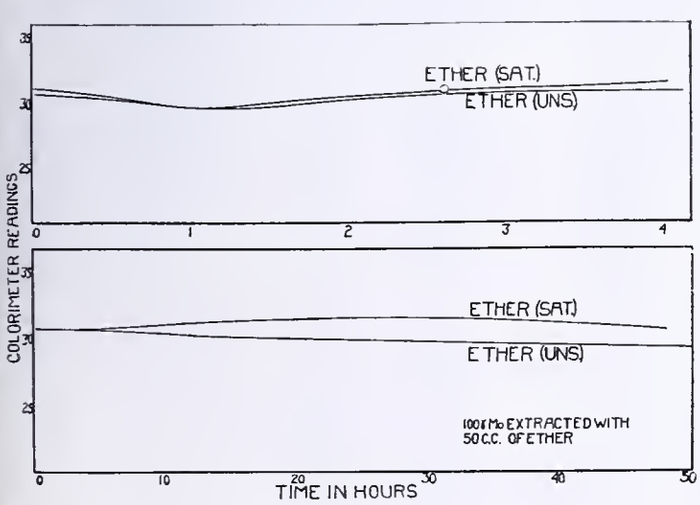

Figure 5

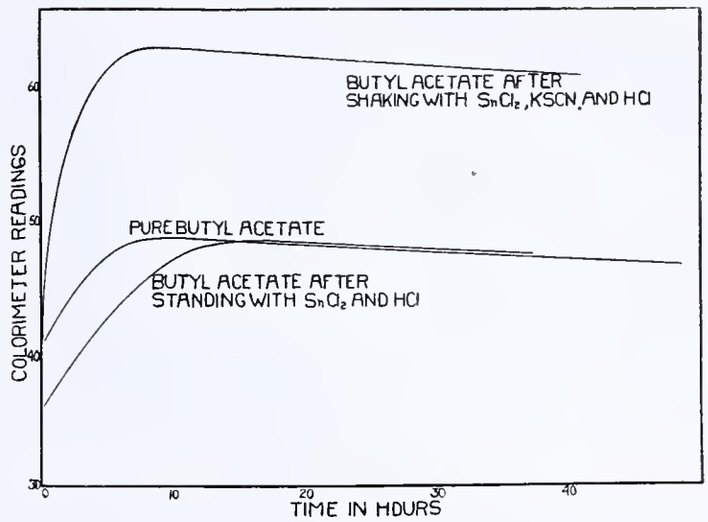

Figure 9

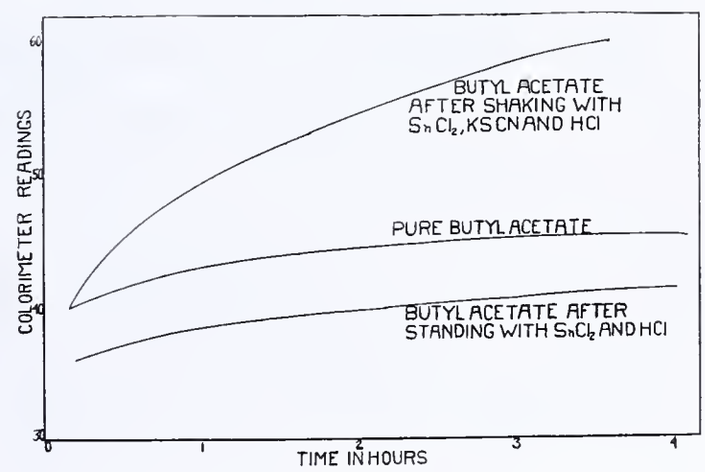

Figure 8

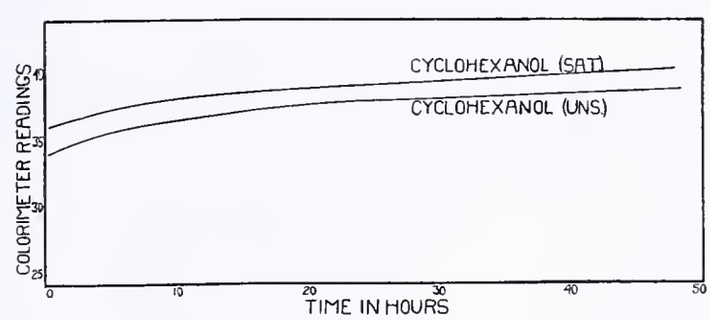

Figure 7

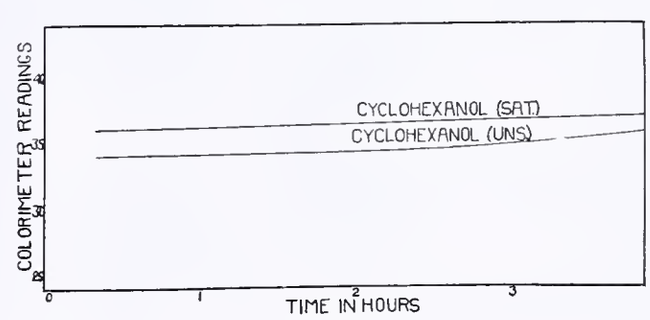

Figure 6

Butyl acetate, although an excellent solvent for the thiocyanate, should be used with care. The color produced by a given concentration of molybdenum appears to depend to no slight extent upon the manner in which the solvent has been saturated with the reagents. Figures 8 and 9 illustrate the type of results obtained with butyl acetate. It will be noted that the solvent which had been shaken with all three reagents changed color rapidly. The color of pure butyl acetate solutions of molybdenum thiocyanate likewise intensified, although not so rapidly or to so marked a degree. Butyl acetate which had been previously saturated with stannous chloride and hydrochloric acid under the conditions of the experiment behaved in a similar manner, although the intensity of the color was less during the first 12 hours.

Summary

Within the limits of the observations it is recommended that in the determination of molybdenum the concentration of hydrochloric acid be held at 5.0 per cent, potassium thiocyanate at 0.6 per cent, and stannous chloride above 0.1 per cent. Under some conditions sulfuric acid exerts an appreciable influence upon the color formation. Extraction of the complex should be made 5 minutes after adding the reagents. The behavior of the thiocyanate in ether, cyclohexanol, and butyl acetate has been studied. Anomalous color effects obtained with butyl acetate indicated that in general it was not as satisfactory an extractor for molybdenum as ether or cyclohexanol.

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An Optical Crystallographic Study of Some Derivatives of Barbital and Luminal

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CHEMICAL tests are not entirely satisfactory for the identification of some barbituric acid derivatives. Of these derivatives, two of the most commonly used are barbital (veronal or 5,5-diethyl barbituric acid) and phenobarbital (luminal or 5-ethyl-5-phenyl barbituric acid) for which optical crystallographic data are here presented. These data can be useful in the identification of these two medicinal substances. None of the derivatives presented in this paper, however, have been reported in the literature with the exception of the *p*-nitrobenzyl compounds, which have been prepared by Lyons and Dox (*3*), Hargreaves and Nixon (*1*), and Jesperson and Larsen (*2*).

Preparation and Analysis

A number of benzyl and phenacyl derivatives were prepared from barbital and phenobarbital in the following manner:

Equivalent amounts of the barbituric acid and potassium or sodium carbonate were dissolved in a little more than enough boiling water to make a saturated solution. This solution was added to a solution of the benzyl or phenacyl halide (two molecular quantities) dissolved in an amount of alcohol twice as large as the amount of water used to dissolve the barbituric acid salt. The resulting mixture was refluxed until the reaction was completed.

The *o*-chlorobenzyl and the phenacyl derivatives of phenobarbital were prepared, but were obtained in the form of oily liquids which could not be made to crystallize. The *p*-chlorobenzyl derivative of phenobarbital occurs in two forms, depending on the method used for purification. If crystallization is caused to take place from a hot saturated solution, form A (Tables I and II) is obtained; but if the crystallization takes place slowly from a less saturated solution, we obtain form B.

Each new compound was analyzed for halogens or nitrogen. The melting points were run by both the tube method and the "Bloc Maquenne" method. Water of crystallization was not present in any of the compounds prepared.

Table I. Derivatives of Barbital and Phenobarbital

Derivative	Formula	Crystal Habit	Color	Halogen Calcd.	Halogen Found[a]	Melting Point Uncorrected Tube	Melting Point Uncorrected Block
				%	%		
			Barbital				
o-Bromobenzyl	$C_{22}H_{22}N_2O_3Br_2$	Thick rods	White	30.62	30.50	140	141
m-Bromobenzyl	$C_{22}H_{22}N_2O_3Br_2$	Thin plates	White	30.62	30.57	91	90
p-Bromobenzyl	$C_{22}H_{22}N_2O_3Br_2$	Flat rods and plates	White	30.62	30.65	146	147
o-Chlorobenzyl	$C_{22}H_{22}N_2O_3Cl_2$	Long rods	White	16.37	16.49	127	125
m-Chlorobenzyl	$C_{22}H_{22}N_2O_3Cl_2$	Thin plates	White	16.37	16.34	102	100.5
p-Chlorobenzyl	$C_{22}H_{22}N_2O_3Cl_2$	Flat rods and plates	White	16.37	16.32	142	144
p-Iodobenzyl	$C_{22}H_{22}N_2O_3I_2$	Rods and thick plates	White	40.55	40.48	122	123
m-Nitrobenzyl	$C_{22}H_{22}N_4O_7$	Long needles	Pale yellow	12.34[b]	12.27[b]	159	160
p-Nitrobenzyl	$C_{22}H_{22}N_4O_7$	Needles and rods	Pale yellow	12.34[b]	12.29[b]	192	193
Phenacyl	$C_{24}H_{24}N_2O_5$	Flat rods and plates	White	6.67[b]	6.72[b]	191	192
p-Bromophenacyl	$C_{24}H_{22}N_2O_5Br_2$	Rods	White	27.65	27.55	191.5	193
			Phenobarbital				
o-Bromobenzyl	$C_{26}H_{22}N_2O_3Br_2$	Short rods	White	28.04	27.98	116	113
m-Bromobenzyl	$C_{26}H_{22}N_2O_3Br_2$	Thin plates	White	28.04	28.14	130	130
p-Bromobenzyl	$C_{26}H_{22}N_2O_3Br_2$	Thin plates, twinned	White	28.04	28.05	117	118
m-Chlorobenzyl	$C_{26}H_{22}N_2O_3Cl_2$	Thin plates	White	14.74	14.90	111	111
p-Chlorobenzyl	$C_{26}H_{22}N_2O_3Cl_2$ A	Thin plates, twinned	White	14.74	14.63	111	111
	B	Thick plates	White	14.74	14.64	113	114
p-Iodobenzyl	$C_{26}H_{22}N_2O_3I_2$	Thick plates and rods	White	37.77	37.90	127–8	127
m-Nitrobenzyl	$C_{26}H_{22}N_4O_7$	Flat rods and plates	Pale yellow	11.16[b]	11.17[b]	149.5	151
p-Nitrobenzyl	$C_{26}H_{22}N_4O_7$	Rods and needles	Yellow	11.16[b]	11.20[b]	182.5	184
p-Bromophenacyl	$C_{28}H_{22}N_2O_5Br_2$	Rods and needles	White	25.53	25.65	164	167

[a] Average of two determinations.
[b] Per cent nitrogen

TABLE II. OPTICAL CRYSTALLOGRAPHIC DATA FOR DERIVATIVES OF BARBITAL AND PHENOBARBITAL

(All monoclinic)

Derivative	Optical Characteristic (Sign)	Sign of Elongation	Refractive Indices at 25° Alpha	Beta	Gamma	Rhombic Dispersions	Extinction Angle, Degrees
			Barbital				
o-Bromobenzyl	−	+	1.556	1.640	1.663	None	16
m-Bromobenzyl	−	+	1.577	1.679	1.693	None	30
p-Bromobenzyl	+	−	1.556	1.577	1.698	None	4
o-Chlorobenzyl	−	+	1.548	1.649	1.696	None	20
m-Chlorobenzyl	−	+	1.538	1.640	1.690	None	23
p-Chlorobenzyl	+	−	1.545	1.563	1.664	None	33
p-Iodobenzyl	+	−	1.531	1.642	$>CH_2I_2$	None	34
m-Nitrobenzyl	−	−	1.487	1.626	1.715	Strong $\nu > \rho$	7
p-Nitrobenzyl	±	+	1.510	1.606	1.706	Strong	14
Phenacyl	−	+	1.587	1.626	1.634	Moderate $\rho > \nu$	42
p-Bromophenacyl	−	+	1.599	1.642	1.649	None	32
			Phenobarbital				
o-Bromobenzyl	+	±	1.605	1.620	1.720	Moderate $\nu > \rho$	36
m-Bromobenzyl	−	−	1.599	1.668	1.698	None	7
p-Bromobenzyl	[a]	+	1.563	[a]	$>CH_2I_2$	[a]	9
m-Chlorobenzyl	−	−	1.580	1.660	1.681	None	5
p-Chlorobenzyl A	[a]	+	[a]	1.568	$=CH_2I_2$	[a]	8
B	+	±	1.585	1.593	1.730	None	15
p-Iodobenzyl	−	±	1.580	1.730	$>CH_2I_2$	Moderate $\nu > \rho$	34
m-Nitrobenzyl	−	+	1.538	1.652	1.715	Moderate $\nu > \rho$	25
p-Nitrobenzyl	−	+	1.534	1.666	$=CH_2I_2$	Strong $\nu > \rho$	17
p-Bromophenacyl	+	−	1.599	1.656	1.703	Strong $\nu > \rho$	36

[a] Since no optic axis interference figure could be seen, these values could not be determined.

Eleven derivatives of barbital and nine derivatives of phenobarbital were prepared, purified, and analyzed. The results are presented in Table I.

OPTICAL CRYSTALLOGRAPHIC DATA. The optical properties of each compound listed in Table I were determined by methods used in a similar study for compounds of strychnine (*4*) and cinchonine (*5*), and are presented in Table II. The optical properties of the derivatives of barbital differ sufficiently from those of phenobarbital to allow the use of the optical data in the identification of the original barbituric acid.

Summary

Ten new derivatives of barbital and eight new derivatives of phenobarbital have been prepared and described. The optical crystallographic data for twenty benzyl and phenacyl compounds of barbital and phenobarbital have been determined.

Acknowledgment

The authors wish to thank the Winthrop Chemical Company, Inc., New York, N. Y., for kindly furnishing the barbital and phenobarbital.

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Surface Tension between Aqueous and Isopropyl Ether Solutions of Acetic Acid

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THE factors determining the rate of extraction of acetic acid from aqueous solution by isopropyl ether and the efficiencies of types of equipment applicable to the extraction operation are under investigation in this laboratory. These form one phase of an investigative program directed toward the development of methods and data for the rational design of liquid-liquid extraction systems. Results thus far obtained show that the rate of extraction and, consequently, the efficiency of liquid-liquid contact equipment in which one solvent phase is dispersed may be primarily influenced by the interfacial surface tension between the two solvents. It is apparent that this result is logically explained by the fact that for a given volume of liquid the degree of dispersion and droplet size (hence contact area) are determined primarily by interfacial surface tension. Since the concentration of the soluble component distributing itself between two immiscible solvents in contact may exert a very considerable influence on their interfacial surface tension, the extent or efficiency of extraction in a given equipment is a function of the respective solute concentrations in the two phases, operating conditions and concentration gradient being otherwise fixed. Thus, in the extraction of acetic acid from water solution by isopropyl ether, the capacity coefficients in a tower of the spray type and the plate efficiencies of a bubble plate column are dependent upon the respective acid concentration of the two phases. A similar result for other types of contacting devices is also to be expected.

To permit a correlation of the results on this system the surface tension of different concentrations of aqueous acetic acid against isopropyl ether of varying acetic acid concentra-

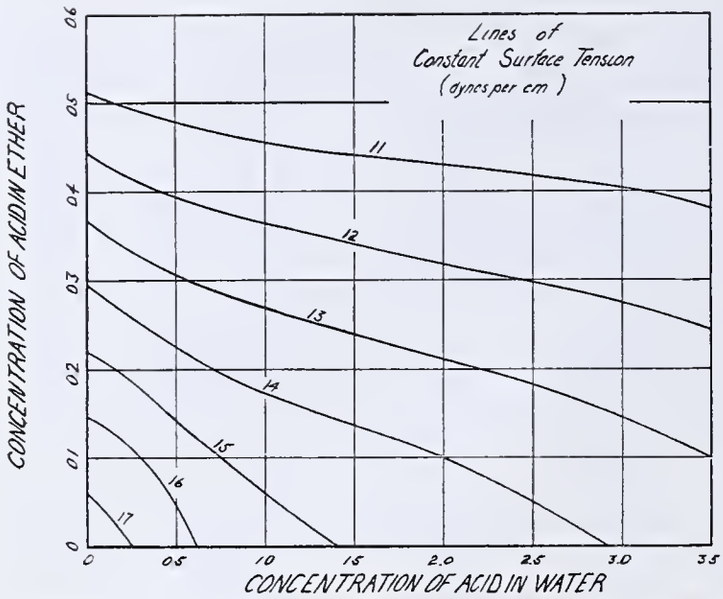

FIGURE 1. SURFACE TENSION BETWEEN WATER AND ISOPROPYL ETHER PHASES CONTAINING ACETIC ACID

Concentrations in gram molecules per liter.

tion has been measured. Inasmuch as this system is the basis of an industrial process for the recovery of acetic acid and no previous data on its surface tension appear to be available, it was thought that the present measurements would be of industrial as well as scientific interest.

Experimental Method

The "drop weight" method of determining surface tension was employed. The procedure followed was based on suggestions advanced by Harkins and Brown (*2*). This method combines simplicity (*1*) with a degree of accuracy commensurate with that to be expected from any usual applications of the results.

The apparatus consisted of a 5-cc. buret attached through a suitable stopcock to a 10-cm. length of 7-mm. capillary tubing. The tip of this was carefully ground, and its diameter accurately determined to be 0.377 mm. The denser phase was placed in the buret and permitted to drop through the less dense at the rate of approximately one drop every 3 minutes. From accurate measurements of the volume of the drops, the densities, and the size of the tip surface tensions were calculated from the usual relation as given in the International Critical Tables.

The accuracy yielded by the apparatus as constructed was checked by comparing values of the surface tensions of water, benzene, and benzene-water obtained with it with the corresponding values reported in the literature. That substantial agreement was obtained may be seen from Table I.

TABLE I. SURFACE TENSION COMPARISON

(Temperature 20° C.)

System	Drop Volume	Density	Surface Tension Observed	Surface Tension Accepted value (*3*)
	Cc.	*G./cc.*	*Dynes/cm.*	*Dynes/cm.*
Water-air	0.1070	0.9972	73.46	72.75
Benzene-air	0.0485	0.8746	28.49	28.80
Benzene-water	0.4500	H_2O-0.9968 C_6H_6-0.8738	34.50	35.00

In making the measurements presented herein aqueous acetic acid of different concentrations was placed in the buret and drops were permitted to form in isopropyl ether solutions of various concentrations. Purified isopropyl ether from the Eastman Kodak Company, distilled water, and U. S. P. acetic acid were employed. Each phase was mutually saturated with the other by agitation for a prolonged period in a thermostat at 20° C. before making measurements. The solutions were removed from the thermostat into a room at approximately 20° C. immediately prior to each determination.

With solutions of different concentrations the drop weight method is superior to the ring method. The latter requires a large surface and consequently allows variation in the respective solution concentrations during measurement due to diffusion across the interface. Use of the drop weight method greatly reduces this effect. Reproducible results were readily obtained by permitting fresh drops to form continuously in a large volume of solution.

Results

The surface tension results obtained are recorded in Table II. Corresponding densities of the aqueous and isopropyl ether solutions of acetic acid employed, each solvent mutually saturated by the other, were also determined since their knowledge was necessary for the calculation of surface tension values. (As reported by the Carbide and Carbon Chemicals Corporation commercial isopropyl ether at 25° C. is soluble in water to the extent 0.65 per cent by volume, water being soluble in the ether to the extent of 0.025 per cent by volume. Pure isopropyl ether is undoubtedly considerably less soluble.) Inasmuch as no previous data on these have been reported the authors' values are also included in the table.

TABLE II. VALUES OF SURFACE TENSION BETWEEN AQUEOUS AND ISOPROPYL ETHER SOLUTIONS OF ACETIC ACID AT 20° C.

Ether Concentration	Water Concentration	Density Ether	Density Water	Drop Volume	Surface Tension
G. moles/l.	*G. moles/l.*	*G./cc.*	*G./cc.*	*Cc.*	*Dynes/cm.*
0.0044	0.0001	0.7246	0.9951	0.0940	17.56
0.0583	0.0001	0.7262	0.9951	0.0914	17.08
0.1718	0.0001	0.7296	0.9951	0.0843	15.66
0.5239	0.0001	0.7399	0.9951	0.0624	10.90
0.0060	0.2519	0.7247	0.9977	0.0900	16.97
0.0581	0.2519	0.7262	0.9977	0.0882	16.54
0.1710	0.2519	0.7295	0.9977	0.0825	15.28
0.5134	0.2519	0.7396	0.9977	0.0604	10.65
0.0092	0.6234	0.7247	1.0008	0.0836	15.95
0.0584	0.6234	0.7262	1.0008	0.0825	15.65
0.1709	0.6234	0.7295	1.0008	0.0776	14.55
0.5009	0.6234	0.7392	1.0008	0.0594	10.60
0.0140	1.5368	0.7249	1.0074	0.0761	14.84
0.0623	1.5368	0.7263	1.0074	0.0751	14.57
0.1716	1.5368	0.7296	1.0074	0.0712	13.73
0.4976	1.5368	0.7392	1.0074	0.0573	10.46
0.0212	3.2513	0.7250	1.0199	0.0676	13.69
0.0679	3.2513	0.7265	1.0199	0.0664	13.39
0.1724	3.2513	0.7296	1.0199	0.0637	12.69
0.4982	3.2513	0.7391	1.0199	0.0539	10.26

By plotting the surface tension exerted between solutions of various concentrations with acid concentration in the ether as ordinates and in water as abscissas as in Figure 1, lines of constant surface tension are obtained. From this graph the surface tension exerted between the two phases for varying acid concentrations may be readily obtained by interpolation.

It is evident that the surface tension between these two immiscible solvents is markedly dependent upon their respective acetic acid concentrations. Consequently, the dispersion of either phase in the other will vary greatly with their respective acid concentrations. These data are of value for predicting qualitatively where other variables are fixed, the area of contact and, consequently, the influence of acid concentration on the extraction efficiency to be expected for the various stages of extraction equipment operating this process.

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Preparation and Properties of Mono-, Di-, and Tricalcium Phosphates

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THE three common phosphates of calcium—namely, the mono-, di-, and tricalcium phosphates—are of great importance because of their usage as fertilizers, their presence in soils, and their use in numerous commercial products. Monocalcium phosphate is the essential constituent of superphosphate fertilizer, which is manufactured to the extent of about 15,000,000 tons annually, and valued at several hundred million dollars. Di- and tricalcium phosphates find a restricted use as fertilizers at present, but this use may increase. Notwithstanding the great importance of these phosphates, information regarding their preparation and properties in pure crystalline form leaves much to be desired. Because samples of pure crystalline material were often not at hand, the results of these determinations of their properties are in many cases open to question. It was for the purpose of preparing these phosphates in pure crystalline form and determining some of the more important properties of these pure forms that this investigation was undertaken.

General Laboratory Methods

Phosphorus was determined by both the colorimetric and gravimetric methods. The colorimetric method followed is that described by Truog and Meyer (*28*). The gravimetric method followed is essentially that given by Treadwell and Hall (*26*), except that a smaller sample (approximately 0.035 gram of P_2O_5) was used, 5 grams of ammonium nitrate were added to each solution previous to precipitation, and the ammonium molybdate solution used was prepared according to official methods (*1*). The colorimetric method was used whenever the amount of phosphorus involved was so small that the gravimetric method could not be used conveniently.

Calcium was determined by precipitation as the oxalate and titration with potassium permanganate.

The loss of water by the salts at different temperatures was determined by heating 1-gram samples in an electric oven for the temperature range of 40° to 185° C., in an electric furnace equipped with a pyrometer for the temperature range of 190° to 800° C., and over Bunsen and Méker burners for temperatures above 850° C.

The carbon dioxide-free water used in solubility studies was prepared by drawing carbon dioxide-free air through distilled water for approximately 48 hours. Throughout this paper, water so treated will be designated as "water." The carbon dioxide-saturated water was prepared by passing carbon dioxide through distilled water until it attained a pH of 3.8.

The solubility studies, unless stated otherwise, were conducted by shaking the suspensions for the designated period, after which they were allowed to stand with intermittent shaking for 24 hours in a water bath maintained at 25° C.

The pH of water solutions of the three phosphates was determined with the hydrogen electrode.

Monocalcium Phosphate Monohydrate

PREPARATION. A review of the literature pertaining to the preparation of pure crystalline monocalcium phosphate monohydrate shows that the ratio of P_2O_5 to CaO (*2*, *24*), temperature at which crystallization takes places (*2*), and kind of washing liquids used (*24*, *25*) are factors to be considered.

Clark (*10*) attempted to prepare the pure salt by dissolving the commercial product in water and evaporating until crystallization had proceeded for some time. Then the mixture was cooled to 50° C. and centrifuged. The ratio of P_2O_5 to CaO of his product was slightly higher than the theoretical, due to the presence of free acid.

In some preliminary trials, the writer was unable to obtain pure crystalline products from solutions evaporated at 40° C. when the ratios of P_2O_5 to CaO were 3 to 1 and 4 to 1. With a ratio of 5 to 1, a pure crystalline product was finally obtained when prepared in the following manner:

To 3 liters of water containing 332 grams of P_2O_5 as phosphoric acid, calcium hydroxide equivalent to 66.4 grams of CaO was added. The filtered solution was evaporated at 35° to 40° C., using an air current to hasten evaporation. The solution was stirred several times a day, and any salt crystallizing on the side of the beaker was pushed down into the solution to dissolve. Crystallization began when the volume had been reduced from 3 liters to approximately 850 cc. The temperature was then lowered to 30° to 33° C. When the volume had been reduced to 500 cc., the supernatant liquid was decanted, the crystalline mass crushed somewhat to liberate occluded phosphoric acid, and the excess liquid removed by suction, using a Büchner funnel. The crystalline mass was washed once by decantation with 800 cc. of absolute alcohol, then transferred to a Büchner funnel with absolute alcohol, and washed six times with 125-cc. portions of absolute alcohol. The suction was stopped before each addition until the alcohol had become well distributed. The crystals were finally washed, similarly, three times with absolute ether, spread onto a sheet of paper, and maintained at a temperature of approximately 25° C. until the ether had evaporated. The salt was ground to pass a 20-mesh sieve, the yield being about 66 per cent of the theoretical. The salt did not take on a tarry odor during a period of one year, which Clark (*10*) found to be the case when he used alcohol and ether for washing his product.

COMPOSITION AND CRYSTAL PROPERTIES. The results of analyses for phosphorus and calcium of the prepared monocalcium phosphate monohydrate are given in Table I, as are also results of analyses of di- and tricalcium phosphates. These analyses show that the salt prepared was pure and a monohydrate. The crystals were white and rhomboidal in shape.

TABLE I. ACTUAL AND THEORETICAL COMPOSITION OF THREE PHOSPHATES PREPARED

Phosphate	Composition: By analysis of those prepared			Composition: Theoretical		
	P_2O_5	CaO	$\frac{P_2O_5}{CaO}$	P_2O_5	CaO	$\frac{P_2O_5}{CaO}$
	%	%		%	%	
$CaH_4(PO_4)_2 \cdot H_2O$	56.65 56.60	22.40 22.25	2.54	56.30	22.12	2.54
$Ca_2H_2(PO_4)_2 \cdot 4H_2O$	41.46 41.14	32.90 33.20	1.25	41.27	32.48	1.27
$Ca_3(PO_4)_2 \cdot H_2O$	42.40 42.50	51.20 51.20	0.83	43.30	51.10	0.84

Results of petrographic examination are given in Table II. The crystals are very finely twinned, but not of the same orientation, thus necessitating the choosing of single crystals for optical work. The x-ray diffraction pattern is represented in Figure 1, and differs markedly from those of di- and tricalcium phosphates, the lines being more prominent than those of the latter phosphate but less so than those of the former.

LOSS OF WATER AND TRANSFORMATION ON HEATING. Results of the effect of heating monocalcium phosphate monohydrate at different temperatures for short and long periods of time on loss of weight are given in Table III. Prolonged

Table II. Crystal Properties of Monocalcium Phosphate Monohydrate and Dicalcium Phosphate Tetrahydrate

Phosphate	Properties of Crystals: System	Sign	Value of $2V$	Refractive indices using "D" light N_g	N_m	N_p
Monocalcium phosphate monohydrate	Triclinic	Minus	70°	1.5292	1.5176	1.4932
Dicalcium phosphate tetrahydrate	Monoclinic	Minus	83°	1.5516	1.5457	1.5394

heating at 100° C. caused a loss in weight equivalent to 0.96 molecule of water (variation from 1 molecule is within limit of error), showing that the molecule of water is lost at a lower temperature than is reported by some investigators (*4, 14*), and that the anhydrous salt is quite stable when heated for long periods of time at this temperature. It is also stable when heated for 5-hour periods over a temperature range of 103° to 153° C.

When the salt was heated at 200° to 205° C. for nearly 10 weeks, it gradually lost weight equivalent to 2.5 molecules of water. This loss can be accounted for by the formation of a mixture of calcium pyrophosphate and metaphosphoric acid in accordance with the equation given by Stoklasa (*24*):

$$2CaH_4(PO_4)_2.H_2O = Ca_2P_2O_7 + 2HPO_3 + 5H_2O\uparrow$$

The mixture thus obtained was dissolved in water acidified with sulfuric acid, and the presence of one or both compounds in solution was shown by the formation of a white precipitate when silver nitrate was added. Pyrophosphate was shown to be present in the mixture by the formation of a white precipitate when zinc sulfate was added in excess to the solution at approximately pH 5.4. A few drops of a water extract of the mixture caused coagulation of a solution of albumin, indicating the presence of metaphosphate.

In order to confirm further the presence of metaphosphate and pyrophosphate, the relative rate of hydrolysis to orthophosphate in boiling water of the mixture obtained by heating and of pure calcium pyrophosphate was investigated.

The relative rate of hydrolysis was studied by boiling 0.05-gram samples in 500 cc. of water for the given period. After cooling, aliquots were filtered and analyzed for orthophosphate by the colorimetric method. The remainder of the unfiltered aliquot was then boiled for the next desired period. The mixture at first hydrolyzed much more rapidly than did a sample of pyrophosphate. The velocity of hydrolysis of the mixture became much slower after an amount of phosphorus equivalent to the calculated amount of metaphosphoric acid had hydrolyzed. This slower velocity was similar to the velocity of hydrolysis of the calcium pyrophosphate alone. This test confirmed the presence of pyrophosphate and metaphosphate in accordance with the reaction just given.

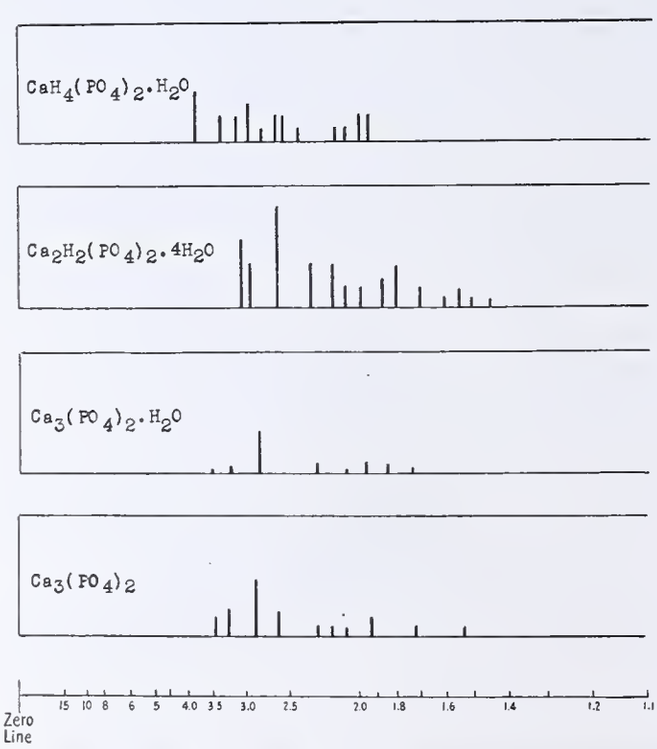

Figure 1. Diagrams of X-Ray Patterns of Phosphates

Length of lines indicates estimated intensity of diffraction spectra lines Mo. radiation. λ = 0.712 Å. R = 20 cm.

Table III. Effects of Temperature and Period of Heating on Loss of Weight of Monocalcium Phosphate Monohydrate

(Loss of 7.14 per cent is equivalent to 1 mole water)

Temperature of Heating	Period Heated	Loss of Weight on Hydrated Salt Basis
° C.	*Hours*	%
99 to 101	27	6.32
90 to 101	256	6.93
90 to 101	334	6.93
103	5	6.73
109	5	7.14
119	5	7.25
134	5	7.31
147	5	7.39
151	5	7.41
203	1	10.83
203	3	11.66
203	18	13.74
203	63	14.91
203	158	15.66
203	254	15.90
203	373	16.27
203	492	16.30
203	587	16.33
203	730	16.40
203	855	16.81
203	974	17.54
203	1165	17.59
203	1362	17.60
203	1658	17.60
325	204	21.78
900 to 910	1/3	22.40
900 to 910	4	23.16
950 to 970	7	23.80
950 to 970	30	33.47
950 to 970	49	36.77
950 to 970	82	40.56
950 to 970	127	42.07
950 to 970	170	42.35
950 to 970	176	42.34

When the monocalcium phosphate monohydrate was heated at 325° C. for 204 hours, a loss in weight equivalent to 3 molecules of water took place. This loss can be accounted for by a complete change from orthophosphate to metaphosphate in accordance with the following equations:

$$2CaH_4(PO_4)_2.H_2O = Ca_2P_2O_5 + 2HPO_3 + 5H_2O$$
$$Ca_2P_2O_7 + 2HPO_3 = Ca_2P_2O_7 + P_2O_5 + H_2O$$
$$Ca_2P_2O_5 + P_2O_5 = 2Ca(PO_3)_2$$

To study the effect of higher temperatures for short and long periods of time, samples of the salt were heated for about 20 minutes, and also for 4 hours, over a Bunsen burner at approximately 900° to 910° C., and then for longer periods over Méker burners at approximately 950° to 970° C. until the weights were constant. The data obtained (Table II) show that at the temperature of a Bunsen burner the equivalent of 3 molecules of water is removed in about 20 minutes, and when the temperature is raised to that of a Méker burner, the equivalent of approximately 3 more molecules of water is removed gradually over a period of 170 hours. The total loss was equivalent to 6 molecules of water. A loss in weight (49.6 per cent) equivalent to 7 molecules of water can be accounted for by the equation:

$$2CaH_4(PO_4)_2.H_2O + \text{heat} = Ca_2P_2O_7 + P_2O_5\uparrow + 6H_2O\uparrow$$

in which case both phosphoric anhydride and water are removed. This is in disagreement with Hinds (*18*), who states that metaphosphate is the final product when monocalcium and dicalcium phosphate are heated. A further loss in

weight equivalent to 1 molecule of water might have taken place at a higher temperature.

Solubility and Reaction. For a review of the literature pertaining to the solubility of monocalcium phosphate monohydrate, the reader is referred to articles by Cameron and Hurst (*7*), Sanfourche and Focet (*22*), Seidell (*23*), and Stoklasa (*24*).

The effect of shaking for different periods of time on the solubility was studied first. The salt was added to water and carbon dioxide–saturated water at the rate of 25 and 50 grams per liter, respectively. The suspensions were placed on a shaker, and aliquots taken after 3, 9, 24, and 48 hours, filtered, and then analyzed for phosphorus. The results are given in Table IV. These data indicate that shaking for 3 hours was sufficient for equilibrium to take place in both solvents.

Table IV. Effects of Period of Shaking and Amount of Salt Added on Solubility of Monocalcium Phosphate Monohydrate in Water and Carbon Dioxide–Saturated Water

(Ratio of P_2O_5 to CaO in salt is 2.53)

Solvent	Period of Shaking	Salt Added	Salt Dissolved According to: Phosphorus in solution		Calcium in solution		Ratio of P_2O_5 to CaO in Solution
	Hours	*G./l.*	*G./l.*	%	*G./l.*	%	
Water	24	10.0	9.92	99.2	10.00	100.0	2.52
	24	12.0	10.80	90.0	11.80	98.3	2.32
	24	20.0	18.90	94.5	18.70	93.5	2.55
	3	25.0	23.85	95.5	...	...	..
	9	25.0	23.85	95.5	...	...	..
	24	25.0	23.85	95.5	...	...	..
	48	25.0	23.85	95.5	...	...	..
	3	40.0	36.60	91.5	...	...	..
	24	100.0	87.17	87.2	79.90	79.9	2.78
CO_2–saturated water	3	14.0	13.97	99.7	13.82	98.8	2.56
	3	14.5	14.50	100.0	14.00	96.5	2.64
	3	16.0	15.40	96.7	15.80	99.0	2.48
	3	17.0	17.00	100.0	16.65	98.0	2.59
	24	20.0	17.80	89.0	19.40	97.0	2.33
	14	25.0	24.70	98.7	23.20	93.0	2.71
	3	50.0	46.80	93.5	...	...	..
	9	50.0	46.80	93.5	...	...	..
	24	50.0	46.80	93.5	...	...	..
	48	50.0	46.80	93.5	...	...	..
	24	75.0	62.00	82.5	61.00	81.3	2.58
	24	100.0	86.70	86.7	77.00	77.0	2.86

The influence of ratio of salt to solvent on solubility was studied by adding 10 to 100 grams of salt to a liter in the case of water, and 14 to 100 grams in the case of carbon dioxide–saturated water. The results of analyses for phosphorus and calcium in solution are given in Table IV, and show that all the added phosphate dissolved when 10 grams of salt were added per liter of water at 25° C. Beyond this, the percentage of salt which dissolved decreased, but the actual amount increased greatly.

In the case of carbon dioxide–saturated water, all the added phosphate dissolved at 25° C. when 14 grams of salt per liter were added. The percentage of salt that dissolved decreased as the quantity of salt added was increased, while the actual amount increased. As the amount of salt added to both solvents increased, the ratio of P_2O_5 to CaO in the solution increased, showing that some decomposition was taking place, and that a more insoluble calcium salt was being formed and left out of solution. Stoklasa (*24*) believed that the process of decomposition could be represented as follows:

$$X\ CaH_4(PO_4)_2.H_2O + H_2O = (X - 1)\ CaH_4(PO_4)_2.H_2O + CaHPO_4 + 2H_2O + H_3PO_4$$

When X equals 4, the undecomposed quantity would be 75 per cent, and the decomposed 25 per cent.

The effect of concentration of monocalcium phosphate monohydrate in filtered water solutions on reaction is shown in Table V. The solution having the highest ratio of P_2O_5 to CaO had the lowest pH. The acidity increased with increasing concentrations of dissolved salt.

Table V. Reaction of Water Solutions of the Three Phosphates

Phosphate	Salt Added	Salt Dissolved, Based on Phosphorus in Solution	pH of Solution
	G./l.	*G./l.*	
Monocalcium phosphate monohydrate	10.0	9.92	3.62
	100.0	87.17	2.49
Dicalcium phosphate tetrahydrate	0.5	0.196	6.00
	1.0	0.16	6.55
Tricalcium phosphate monohydrate	0.5	0.0137	6.22
	5.0	0.0307	6.41

Dicalcium Phosphate Tetrahydrate

Preparation. A review of the literature pertaining to the preparation of dicalcium phosphate tetrahydrate indicates that the temperature at which evaporation takes place (*3*, *6*) and the use of proper washing solutions (*13*) are the most important factors to be considered.

The writer prepared the pure crystalline salt in accordance with the method outlined by DeSchulten (*13*). Anhydrous commercial dicalcium phosphate was dissolved in 25 per cent acetic acid solution at 50° C. The filtered solution was evaporated at 25° to 33° C. under a hood, where circulation was aided with a fan. The salt which collected on the side of the beaker was pushed down into the solution. When about 75 per cent of the added salt had crystallized, the crystals were crushed somewhat and the liquid filtered off. The crystalline mass was then washed by decantation ten times with absolute alcohol and finally five times with absolute ether. After drying at room temperature, the crystals were ground to pass a 20-mesh sieve and the product used for determinations of properties.

Composition and Crystal Properties. The results of analyses of the dicalcium phosphate tetrahydrate for phosphorus and calcium are given in Table I, and agree well with the theoretical values of the tetrahydrate salt.

The crystals were pale yellow rhomboidal plates with the sharper corners broken off in many instances, which is in agreement with the observations of DeSchulten (*13*). Results of examination of the crystals under the petrographic microscope are given in Table II, and check very closely with those of Koehler (*19*).

The x-ray diffraction pattern of this salt represented in Figure 1 had more prominent lines than those of the other salts, and it also differed in position of the lines.

Loss of Water and Transformation upon Heating. Results of the effect of heating dicalcium phosphate tetrahydrate for long periods of time at temperatures of 40°, 75°, 110°, 200°, and 950° to 970° C. are given in Table VI. When the salt was heated for approximately 690 hours at 40° C., a loss equivalent to 0.6 molecule of water resulted. The salt gradually lost 1.5 molecules of water when heated at 108° C. for approximately 270 hours. Almost maximum loss occurred within 5 hours when it was heated at 200° C., only a slight additional loss occurring upon further heating, which shows that the salt reaches a stable point quickly at this temperature. When it was heated at 950° to 970° C. for 27 hours, a loss equivalent to nearly 5 molecules of water occurred, which can be accounted for by transformation to the pyrophosphate.

The salt was also heated for short periods—that is, for 5 hours—at temperatures ranging from 40° to 325° C. The results are given in Table VI. There was a gradual loss of water with rise in temperature. The partially hydrated salt was not stable over any temperature range between 40° and 200° C. The first 2 molecules of water were gradually

TABLE VI. EFFECTS OF TEMPERATURE AND PERIOD OF HEATING ON LOSS OF WEIGHT OF DICALCIUM PHOSPHATE TETRAHYDRATE

(Loss of 5.23 per cent is equivalent to 1 mole of water)

Temperature of Heating	Period Heated	Loss of Weight on Hydrated Salt Basis
° C.	Hours	%
40	5	0.08
40	48	0.60
40	96	0.78
40	192	1.89
40	312	2.35
40	621	3.23
40	687	3.57
66	5	1.32
75	15	2.08
75	36	2.70
75	60	3.07
75	108	3.58
75	352	3.52
85	5	2.15
95	5	3.95
105	5	4.87
108	5	5.57
108	11	5.81
108	57	6.41
108	151	7.04
108	270	7.56
108	335	7.60
110	5	6.07
134	5	7.70
150	5	10.45
175	5	13.66
184	5	19.80
200	12	19.57
200	24	19.63
200	49	19.70
230	5	19.80
255	5	19.97
277	5	20.03
310	5	20.25
325	5	20.41
950 to 970	1	25.61
950 to 970	9	25.76
950 to 970	27	25.80

driven off over the temperature range of 40° to 150° C. There was some indication that the third and fourth molecules are removed at the same temperature, or at least within a narrow range of temperature. The first molecule of water was driven off at approximately 108° C., the second at 150° C., and the third and fourth at 150° to 185° C. Dragunov (*14*) reported a loss equivalent to nearly 4 molecules of water by heating the dry salt at 150° C. for only 20 minutes. Davies (*12*) also observed that there was no definite temperature at which the salt lost its water of crystallization.

SOLUBILITY AND REACTION. For a review of the literature pertaining to the solubility of dicalcium phosphate tetrahydrate, the reader is referred to the articles by Cameron and Seidell (*8*), and Cameron and Hurst (*7*).

The effect of duration of period of shaking on solubility was studied first. The salt was added to water and to carbon dioxide–saturated water at rates of 0.12 and 1 gram per liter, respectively. The suspensions were placed on the shaker and aliquots taken after 3, 9, 24, 48, 72, and 96 hours. Results of analyses for phosphorus in the filtered solutions are given in Table VII. Equilibrium was attained after the solutions had been shaken for 72 hours, which is a much longer period than was required by monocalcium phosphate.

The influence of ratio of salt to solvent on solubility was next investigated. Different amounts of salt ranging from 0.12 to 1 gram per liter were added to water, and amounts ranging from 0.266 to 5 grams per liter were added to carbon dioxide–saturated water. The results of analyses for phosphorus and calcium in filtered solutions are given in Table VII. Maximum solubility in water at 25° C. was attained with only 0.5 gram of salt per liter. The ratios between the amounts of phosphorus and calcium which dissolved show that some hydrolysis took place. Approximately 0.2 gram per liter of the salt is soluble in water according to the phosphorus determination. These results are higher than those reported by Seidell (*23*), and lower than those reported by Comey and Hahn (*11*).

The solubility of the salt in carbon dioxide–saturated water was found to be highest when 3 or 4 grams of salt were added per liter. A slightly lower solubility was found when 5 grams per liter were added. Slightly larger proportionate amounts of calcium than of phosphorus were dissolved. These results differ from those obtained in water where larger proportionate amounts of phosphorus than of calcium were dissolved. It is not apparent why the solubility was less when 5 grams of salt were added per liter than when 3 or 4 grams were added. These results for carbon dioxide–saturated water are higher than those given by both Seidell (*23*) and Comey and Hahn (*11*). The ratio of P_2O_5 to CaO in solution agreed better with the formula requirements in the case of carbon dioxide–saturated solutions than in the case of water solutions, indicating less hydrolysis in the former.

TABLE VII. EFFECTS OF PERIOD OF SHAKING AND AMOUNT OF SALT ADDED ON SOLUBILITY OF DICALCIUM PHOSPHATE TETRAHYDRATE IN WATER AND CARBON DIOXIDE–SATURATED WATER

(Ratio of P_2O_5 to CaO in salt is 1.27)

Solvent	Period of Shaking	Salt Added	Salt Dissolved According to: Phosphorus in solution		Calcium in solution		Ratio of P_2O_5 to CaO in Solution
	Hours	G./l.	G./l.	%	G./l.	%	
Water	3	0.12	0.037	30.8	....	..	..
	9	0.12	0.044	36.7	....	..	..
	24	0.12	0.057	47.5	....	..	..
	48	0.12	0.061	50.7	....	..	..
	72	0.12	0.067	55.7	....	..	..
	96	0.12	0.067	55.7	....	..	..
	72	0.50	0.179	36.0	0.139	27.8	1.65
	72	0.50	0.196	39.2	0.128	25.6	1.94
	72	1.00	0.160	16.0	0.135	13.5	1.50
CO_2–saturated water	3	0.266	0.132	49.5	0.133	50.0	1.26
	3	0.570	0.219	38.5	0.243	42.7	1.14
	3	1.0	0.513	51.3	....	..	..
	9	1.0	0.610	61.0	....	..	..
	24	1.0	0.750	75.0	....	..	..
	48	1.0	0.660	66.0	....	..	..
	72	1.0	0.777	77.7	....	..	..
	96	1.0	0.777	77.7	....	..	..
	72	3.0	0.820	27.3	0.8400	27.9	1.24
	72	4.0	0.818	20.5	0.8460	21.1	1.23
	72	5.0	0.685	13.7	0.7200	14.4	1.21

The effect of concentration of dicalcium phosphate in water solutions on the reaction is shown in Table V. The solutions of highest concentration had the lowest pH. Another factor that probably affected the values was the ratios of P_2O_5 to CaO in solution. The pH values of dicalcium phosphate solutions, as would be expected, are much higher than those of the monocalcium phosphate. Zinzadze (*31*) obtained a pH of 7.5 for a freshly prepared solution.

Tricalcium Phosphate Monohydrate

PREPARATION. A review of the literature pertaining to the preparation of tricalcium phosphate monohydrate shows that a pure salt will precipitate in an alkaline solution when the theoretical ratio of P_2O_5 to CaO is present (*29*, *30*), and in an acid solution but above pH 5.5 if a very low ratio of P_2O_5 to CaO is present (*5*).

Tricalcium phosphate monohydrate was prepared as follows in approximately 15-gram quantities:

Sixteen and four-tenths grams of disodium phosphate ($Na_2HPO_4.12H_2O$) were dissolved in 2 liters of water contained in a 3-liter round-bottomed flask. An equivalent quantity of calcium chloride was dissolved in 750 cc. of water and placed in a separatory funnel connected to the mouth of the flask. The stopcock of the funnel was so adjusted that the contents flowed into the flask in about 48 hours. The flask was supported in a water bath maintained at 65° to 70° C., and the contents were kept agitated by means of a stream of carbon dioxide-free air which entered through a fine capillary that extended to the bottom of the flask. During the course of a day, approximately 500 cc. of water evaporated, necessitating the addition of a like amount. Special care was taken to maintain the pH between 7 and 8 by

adding dilute ammonium hydroxide as required. At the end of 48 hours, the precipitate was allowed to settle and the supernatant liquid poured off. Twelve portions were prepared in this manner, mixed together, and the mass washed free of chlorides by decantation, using small quantities of water. The salt was air-dried and ground to pass a 20-mesh sieve, and then used for determinations of its properties.

Composition and Crystal Properties. Results of analyses for phosphorus and calcium of tricalcium phosphate monohydrate are given in Table I, and agree well with the theoretical values of the monohydrate.

The crystals were too small for petrographic study, but x-ray diffraction patterns of both freshly prepared salt and of salt which had been heated for 25 hours at 950° to 970° C. were obtained, and are represented in Figure 1. The lines in the pattern of the heated salt were closer together and were also more prominent than those of the freshly prepared salt, which shows that the molecular planes in the crystal were brought closer together when the crystal was heated. Since in these patterns a number of the prominent lines of mono- and dicalcium phosphate were absent the crystalline properties exhibited were not due to admixtures of mono- and dicalcium phosphates. The exhibition of crystalline properties by tricalcium phosphate monohydrate is in agreement with the work of Zinzadze (*31*) and Gerlach (*17*). Cameron and Seidell (*8*), working prior to the advent of the x-ray method, were unable to establish the crystalline nature of this salt. These patterns, as would be expected, differ from those which Tromel (*27*) obtained for oxyapatite and hydroxyapatite.

Loss of Water and Transformation on Heating. Results of heating tricalcium phosphate monohydrate for short and long periods of time are given in Table VIII. When the salt was heated for 5-hour periods at 65° and 100° C., the loss in weight was very small. This stability of the salt at temperatures around 100° C. was also observed by Zinzadze (*31*). The salt lost weight equivalent to 0.91 molecule of water when heated at 950° to 970° C. for 5 hours. An additional loss of only 0.06 water molecule took place when the same samples were heated for 21 hours more at this high temperature, which is in agreement with the results of Sanfourche (*21*).

Table VIII. Effects of Temperature and Period of Heating on Loss of Weight of Tricalcium Phosphate Monohydrate

(Loss of 5.48 per cent is equivalent to 1 mole of water)

Temperature of Heating	Period Heated	Loss of Weight on Hydrated Salt Basis
° C.	*Hours*	%
65	5	0.60
108	5	0.96
325 to 335	24	3.03
950 to 970	5	4.96
950 to 970	14	5.15
950 to 970	21	5.24
950 to 970	25	5.24

Solubility and Reaction. The influence of ratio of salt to solvent on solubility of tricalcium phosphate monohydrate was studied by Cameron and Seidell (*9*), and Cameron and Hurst (*7*), while Gaarder (*16*), and Osugi et al. (*20*) studied the effect of reaction of the solution on solubility of the salt.

In order to study the effect of period of shaking on solubility, the salt was added to water and to carbon dioxide–saturated water at rates of 0.008 and 0.3 gram per liter, respectively. The suspensions were shaken and samples taken after 3, 9, 24, 48, 72, 96, and 120 hours, filtered, and then analyzed for phosphorus. The results are given in Table IX. The water solutions and the carbon dioxide–saturated solutions came to equilibrium at the end of 96 and 3 hours' shaking, respectively.

Table IX. Effects of Period of Shaking and Amount of Salt Added on Solubility of Tricalcium Phosphate Monohydrate in Water and Carbon Dioxide–Saturated Water

(Ratio of P_2O_5 to CaO in salt is 0.84)

Solvent	Period of Shaking	Salt Added	Salt Dissolved According to: Phosphorus in solution		Calcium in solution		Ratio of P_2O_5 to CaO in Solution
	Hours	*G./l.*	*G./l.*	%	*G./l.*	%	
Water	3	0.008	0.0015	18.7	....	...	..
	9	0.008	0.0018	22.5	....	...	..
	24	0.008	0.0024	30.0	....	...	..
	48	0.008	0.0036	45.0	....	...	..
	72	0.008	0.0040	50.0	....	...	..
	96	0.008	0.0048	60.0	....	...	..
	120	0.008	0.0048	60.0	....	...	..
	24	0.111	0.0097	8.7	....	...	..
	120	0.500	0.0137	2.7	0.0237	4.7	0.49
	48	1.110	0.0158	1.4	....	...	..
	120	5.000	0.0307	0.61	0.0241	0.48	1.06
CO_2–saturated water	24	0.121	0.058	48.0	0.060	49.5	0.81
	3	0.300	0.1480	49.3	....	...	..
	9	0.300	0.1480	49.3	....	...	..
	24	0.300	0.1480	49.3	....	...	..
	24	0.300	0.1420	47.4	0.145	48.5	0.82
	3	0.500	0.1480	29.6	0.149	29.8	0.84
	24	1.000	0.1970	19.8	0.204	20.4	0.82
	24	2.000	0.2010	10.1	0.217	10.8	0.79
	24	4.000	0.2300	5.75	0.235	5.9	0.82

The influence of ratio of salt to solvent on solubility was studied by adding from 0.008 to 5 grams of salt in the case of water, and 0.12 to 4 grams in the case of carbon dioxide–saturated solutions. The results of analyses for phosphorus and calcium are given in Table IX. The maximum solubility of the salt at 25° C. in water was 0.031 gram per liter on the basis of the phosphorus in solution, when 5.0 grams of salt per liter were added. Since more phosphorus than calcium dissolved, the residue, of necessity, became a more basic phosphate than tricalcium phosphate. Cameron and Hurst (*7*) obtained similar results.

The maximum solubility of tricalcium phosphate monohydrate in carbon dioxide–saturated water was approximately 0.23 gram of salt per liter on the basis of the phosphorus in solution, and slightly higher on the basis of the calcium in solution. This solubility was attained when 4 grams of salt were added to a liter of carbon dioxide–saturated water. The ratio of P_2O_5 to CaO in solution was very close to that of the formula. The solubility obtained is within the limits given by Seidell (*23*).

The effect of concentration of the salt in water solutions on reaction is given in Table V. These solutions had higher pH values than solutions of the monocalcium phosphate, but approximately the same as solutions of dicalcium phosphate. The values obtained are slightly lower than those of Zinzadze (*31*), who observed a pH of 6.8 in water solution.

Additional Comments on Reactions of the Three Phosphates

Contrary to first thought, it is to be noted that, depending on the conditions of the test, tricalcium phosphate may apparently give a slightly more acid reaction than dicalcium phosphate. This may be due to the formation of intermediate products or to insufficient time for equilibrium to be established. In order to obtain some further data on the reaction of these phosphates as they are commonly obtained, samples of such commercial products and others as were at hand were tested. In making these tests, 0.2 gram of the phosphate was placed in 20 cc. of carbon dioxide–free water, the suspension shaken 2 minutes, centrifuged, and the pH determined colorimetrically on 5 cc. of the clear supernatant liquid. The results are given in Table X. The pH of the different samples of the mono- and dicalcium phosphates did not vary greatly, as did the samples of tricalcium phosphate. Here again, the samples of tricalcium phosphate usually reacted more acid than did those of dicalcium phosphate.

Table X. Reaction of Various Samples of Three Phosphates

Monocalcium Phosphate	pH
Author's preparation	4.3
Commercial preparation No. 1	3.3
Commercial preparation No. 2	3.0
Research laboratory preparation	3.1
Dicalcium Phosphate	
Author's preparation	7.3
Commercial preparation No. 1	7.2
Commercial preparation No. 2	6.9
Commercial preparation No. 3	6.8
Commercial preparation No. 4	7.0
Research laboratory preparation	6.8
Tricalcium Phosphate	
Author's preparation	6.6
Commercial preparation No. 1	3.6
Commercial preparation No. 2	5.4
Commercial preparation No. 3	6.6
Research laboratory preparation	6.9

Summary

The purpose of this investigation was to prepare mono-, di-, and tricalcium phosphates in pure crystalline form, and to establish the more important properties of these pure forms. The results are summarized as follows:

1. Crystalline monocalcium phosphate monohydrate was prepared by evaporating at 33° to 40° C. a water solution of phosphoric acid and calcium hydroxide having a P_2O_5 to CaO ratio of 5 to 1. The values of the refractive indices N_g, N_m, and N_p were found to be 1.5292, 1.5176, and 1.4932, respectively. It became anhydrous at 109° C., became a mixture of pyrophosphate and metaphosphate on heating for a long period at 203° C., was transformed into metaphosphate at 325° C., and lost weight equivalent to 6 molecules of water at 950° C. The solubility at 25° C. was 10 and 14 grams per liter in water and carbon dioxide–saturated water respectively, when the amount of salt added was limited to that which dissolved completely. However, when more salt was added than would dissolve, hydrolysis was evident. The pH of a water solution containing 10 grams of salt per liter was 3.62.

2. Dicalcium phosphate tetrahydrate was prepared according to the method of DeSchulten—that is, crystallization of the salt at 30° C. from a 25 per cent acetic acid solution to which anhydrous dicalcium phosphate had been added. The refractive indices N_g, N_m, and N_p were found to be 1.5576, 1.5457, and 1.5392, respectively. Heating the salt for 5-hour periods at 108°, 150°, and 150° to 185° C. caused a loss equivalent to 1 molecule, 2 molecules, and 3 to 4 molecules of water, respectively. It was transformed into pyrophosphate at 950° to 970° C. The solubility in water at 25° C. was in the range of 0.16 to 0.196 gram per liter, and in carbon dioxide–saturated water, 0.62 to 0.82 gram per liter. The pH values of water solutions containing 0.196 and 0.160 gram of salt per liter were 6.00 and 6.55, respectively.

3. Tricalcium phosphate monohydrate was prepared by the slow addition of calcium chloride solution to a constantly agitated alkaline solution of disodium phosphate, maintained at 65° to 70° C. An x-ray diffraction pattern indicated the product to be crystalline, but the crystals were too small for petrographic study. The salt was stable at 100° C. When heated at 325° C. for 24 hours and at 950° to 970° C. for 5 hours, it lost weight equivalent to 0.6 and 1 molecule of water, respectively. The solubility in water at 25° C. varied with the ratio of salt to water from less than 0.005 to more than 0.03 gram per liter, and in carbon dioxide–saturated water from 0.058 to 0.23 gram per liter. The pH values of water solutions containing 0.0132 and 0.0307 gram of salt per liter were 6.22 and 6.41, respectively.

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Determination of Total and Free Selenium in Vulcanizates

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THE use of selenium as a vulcanizing agent in rubber stocks has increased considerably during the last few years. Only a small portion of the selenium combines with rubber, whereas the greater part remains free. When analyzing compounds containing selenium, it is interesting to determine selenium in both states. In spite of the available literature, there exist few specific methods of analyzing rubber containing selenium and no method of determining free selenium. The purpose of this paper is to give a method of determining free and total selenium in rubber compounds.

Determination of Total Selenium

Most methods of determining selenium involve treatment of the compound with oxidizing agents, such as hydrogen peroxide, nitric acid, or a mixture of hydrochloric and nitric acids. The selenious acid obtained is reduced to metallic selenium which may be determined by gravimetric, volumetric, or colorimetric methods.

The work of Blake (*2*) and of Shaw and Reid (*4*) outlines methods of determining selenium in rubber. The first involves oxidizing the rubber according to Carius and determining the selenium by iodometric titration. In the second method the rubber is oxidized by fusion with a mixture of sugar, potassium nitrate, and sodium peroxide.

In unpublished work, E. N. Korsunskaya has determined selenium in rubber compounds by oxidizing with nitric acid and reducing the selenious acid with hydrazine sulfate. The latter method seemed to be the simplest, and has been tested on a rubber stock of the following composition:

Formula of Rubber Stock No. 1	
Smoked sheets	100
Zinc oxide	5
Stearic acid	1.5
Captax	0.7
Selenium	3
Sulfur	0.5
	110.7

The determination was accomplished in the following manner:

Two grams of rubber, cut into small pieces, were placed in a 250-cc. Erlenmeyer flask connected to a reflux condenser by a ground joint. Nitric acid (specific gravity 1.4) was introduced in portions of 3 to 4 cc. The flask was heated carefully with a small flame until complete destruction of rubber took place. After cooling, the solution was diluted with water to 150 to 200 cc. The precipitate (nitrosites) formed during this operation was filtered and washed several times with hot water. The filtrate was neutralized with 10 per cent aqueous ammonia and acidified slightly with hydrochloric acid (according to Wagenmann and Triebel, *5*, precipitation with hydrazine sulfate is more satisfactory in dilute hydrochloric acid). The flask containing the solution was then connected with a reflux condenser and 75 to 100 cc. of saturated aqueous hydrazine sulfate were added. For complete precipitation a small excess must be used.

The mixture was carefully heated until the selenium was converted to the black modification. After standing overnight the residue was filtered on a glass Schott's filter and washed with hot water until free of chloride and sulfate, then with alcohol and ether, and afterwards dried at 75° to 80° C. to constant weight (15 to 20 minutes).

The results of the experiments are shown in Table I, experiment A.

As shown in Table I, the results of parallel determinations check. Experimentally, this method is very simple, but the use of the large amounts of hydrazine sulfate is expensive. Besides hydrazine sulfate, such reducing agents as tin chloride, sulfur dioxide, etc., may be used. In using these reducing agents, nitric acid must first be removed. The work of Barkovsky and Babalova (*1*) shows that no losses of selenium occur in evaporating nitric acid from such a solution. The authors have checked this.

After the destruction of the rubber by nitric acid, the mixture was washed into a porcelain cup and evaporated on a water bath until nearly dry. The residue was diluted with 100 cc. of hot water. After being cooled, the solution was filtered and placed in a 500-cc. Erlenmeyer flask. Two hundred and fifty cubic centimeters of hydrochloric acid (specific gravity 1.19) were added, and to this solution crystalline sodium sulfite was introduced in small portions. After each addition the flask was closed by a watch glass. A small surplus of sodium sulfite was introduced when the solution began to turn red. The flask was connected to a reflux condenser, heated to 40° to 50° C., and allowed to stand overnight. Considerable sodium salts precipitate but owing to their ready solubility in water, the determination of selenium is not affected.

The solution was poured through a filter and hot water added to the precipitate of selenium and sodium salts to dissolve the latter. Further filtration, washing, and drying were performed in the regular way.

Table I, experiment B, shows the results obtained by this method.

TABLE I. DETERMINATION OF SELENIUM IN COMPOUND 1

Experiment	Method of Precipitation	Amount of Selenium Calculated	Amount of Selenium Found
		%	%
A	Reducing with hydrazine sulfate	..	2.66
		2.71	2.68
B	Reducing with sulfur dioxide	..	2.58
		..	2.62
		..	2.69

Determination of Free Selenium

In developing a method of determining free selenium, detailed studies of the solubility of selenium were made. The authors tested chloroform, ether, benzene, acetone, carbon bisulfide, and carbon tetrachloride, with negative results.

Selenium dissolves in aqueous potassium cyanide, sodium sulfide, and sodium sulfite, giving chemical compounds. Potassium cyanide gives potassium selenocyanide. Sodium sulfide forms a selenosulfide and sodium sulfite gives a compound of the hyposulfite type. Selenium can be separated easily in its elementary state from each of the above solutions.

Potassium cyanide was discarded because of its poisonous character.

Sodium sulfide solutions had a tendency to separate free sulfur, which necessitated the use of a long and involved procedure.

One hundred cubic centimeters of sodium sulfite solution dissolve 0.1 gram of selenium after refluxing for 2 hours. The filtered and cooled solution on acidification with hydrochloric acid precipitates selenium which may be separated and weighed. In treating rubber in this manner free sulfur is also extracted, which precipitates with the selenium on acidification with hydrochloric acid. The authors have

tested with success the possibility of using formalin for the selective precipitation of selenium. The use of sodium sulfite and formalin permits simultaneous determination of free selenium and free sulfur, the latter by the method of Bolotnikof and Gurova (*3*), which consists of iodometric titration of the hyposulfite formed.

This method has been tested on three mixtures of commercial selenium and sulfur, with the results shown in Table II.

Table II. Determination of Selenium and Sulfur in Mixtures

Selenium Taken	Selenium Found		Sulfur Taken	Sulfur Found	
Gram	*Gram*	%	*Gram*	*Gram*	%
0.1514	0.1492	98.5	0.0648	0.0605	93.4
0.1442	0.1431	98.8	0.0201	0.0190	94.5
0.1700	0.1685	99.1	0.0190	0.0180	94.5

The method of determining free selenium by means of extracting it with sodium sulfite has been checked by the authors on several rubber stocks, compounds 1, 2, and 3. The rubber was milled and cut into pieces 1 mm. square with scissors. Two different curves of No. 1 were used.

	Rubber Formulas	
	No. 2	No. 3
Smoked sheets	100	100
Zinc oxide	5	...
Synthetic rubber	...	100
Stearic acid	1	3
Captax	0.5	1.4
Selenium	3	6
Sulfur	2	1
	111.5	211.4

When using the authors' method of degradation, approximately 30 hours are required to extract free selenium from rubber, the greater part of the selenium being extracted during the first 12 hours.

For determining free selenium, about 1 gram of rubber was placed in a 500-cc. Erlenmeyer flask, 200 cc. of 10 per cent sodium sulfite solution were added, and the mixture was boiled under reflux for 30 hours. A second treatment of the rubber was made with a fresh portion of sulfite solution to insure complete extraction. After cooling, the solution was filtered and the rubber washed with hot water. The flask containing the filtrate was again connected with the condenser, 75 cc. of formalin were added, and the solution was boiled for about an hour. After settling, the selenium was filtered on a Schott's filter and rinsed with water. The filtrate was transferred to another flask and the free sulfur determined. The residue on the filter was washed with hydrochloric acid and hot water until free of chlorides, then with alcohol and ether, and dried to constant weight.

Table III gives a summary of the determination of free selenium in these rubber compounds.

Table III. Determination of Free Selenium in Rubber Stocks

Rubber	Time of Cure	Selenium (Calculated)	Free Sulfur Found	Free Selenium Found	Combined Selenium by Difference
	Min.	%	%	%	%
1	15	2.71	..	2.38	0.33
		2.71	..	2.36	0.35
	40	2.71	..	2.17	0.54
		2.71	..	2.15	0.56
2	..	2.69	0.15	2.29	0.40
			0.16	2.30	0.39
3	..	2.84	0.15	2.27	0.57
			0.18	2.15	0.69

Conclusions

The total selenium in rubber compounds may be determined by disintegrating with nitric acid and then separating the selenium by reducing the nitric acid solution with hydrazine sulfate, or by reducing with sulfurous acid after evaporation of the nitric acid. Free selenium is determined by extracting the rubber with aqueous sodium sulfite, from which selenium is precipitated by formalin.

Free sulfur is determined volumetrically by iodometric titration after precipitating selenium from sulfite solution.

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Colorimetric Determination of Manganese in the Presence of Titanium

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The manganese content of crystalline rocks, according to Hillebrand (*1*), rarely exceeds 0.3 per cent. Long experience with soils in this laboratory shows the manganese content in the average soil of the United States to be about 0.05 to 0.06 per cent. When present in such small quantities manganese is usually determined by a colorimetric method, and the procedure generally used is oxidation to permanganic acid by means of ammonium persulfate. The method for soils commonly used in this laboratory (*2*) is as follows:

One gram of the soil is ignited in a small platinum dish to destroy organic matter, and is then digested on the hot plate with 25 cc. of hydrofluoric acid and 5 cc. of sulfuric acid until white fumes appear. It is cooled, diluted with water, warmed gently until all salts are in solution, and then filtered through a close filter to insure a perfectly clear solution. The filtrate is transferred to a 100-cc. volumetric flask, 1 cc. of 0.5 per cent silver nitrate solution is added, and then 1 gram of ammonium persulfate. The flask is put on the steam bath for 20 to 30 minutes until the color is fully developed. It is then cooled, made up to volume, and compared with a suitable standard in a colorimeter.

Another convenient way to prepare the sample is to fuse, after ignition, with about 10 grams of potassium pyrosulfate and 1 gram of sodium fluoride; heat to fumes for some time, cool, extract with hot water, boil, filter, and treat as above with persulfate. The standard manganese solution is best prepared from c. p. manganese sulfate, and for soils and rocks should have a value of about 0.0002 gram MnO per cubic centimeter.

It is not good practice to take the theoretical percentage of manganese in the manganese sulfate as purchased, as the amount of water held by the salt is variable. Therefore the actual percentage of manganese should be determined gravimetrically, preferably as the phosphate.

It is perhaps not generally known that if titanium oxide is present in the solution in amounts exceeding 1 per cent, the persulfate method is useless, as no color is developed unless excessive amounts of reagents are used, and even then one cannot be certain that the full color has developed. This

was observed recently during the analysis of some soils that were unusually high in titanium (2 to 12 per cent). In making the determination of manganese by the persulfate method no color developed at first, although there was good reason for believing that the samples contained some manganese. When more reagents were added, to an excess of four or five times the usual amount, the color finally appeared.

In order to verify the interference of titanium, which also reacts with persulfates, a sulfuric acid solution containing 54 mg. of titanium oxide and 0.2 mg. of manganese oxide was treated in the usual manner, using 1 gram of ammonium persulfate; no color developed. It should be noted here that ammonium persulfate, with or without silver nitrate, produces the characteristic brown color with titanium only in concentrated solutions strongly acid with sulfuric acid.

When it was found that titanium interfered seriously with the ammonium persulfate method, an attempt was made to eliminate the titanium to avoid its interference. Certain textbooks state that titanium is volatilized by evaporation with hydrofluoric acid unless sulfuric acid or some other acid is present. This statement is not entirely accurate, as shown by the following experiments:

A solution containing 28 mg. of titanium oxide was precipitated by ammonia, filtered, and washed; the precipitate was then evaporated twice to dryness with 20 cc. of hydrofluoric acid. The residue was redissolved in acid, and the titanium determined gravimetrically; 24.2 mg. of titanium oxide were found.

One gram of a soil colloid sample which contained 4.51 per cent of titanium oxide (determined by the color method) was evaporated twice to dryness with 25 cc. of hydrofluoric acid. The residue was then fused with potassium pyrosulfate, and titanium determined gravimetrically by the sulfurous acid method; 4.63 per cent of titanium oxide was found.

One hundred milligrams of finely ground rutile were evaporated three times to dryness with 25 cc. of hydrofluoric acid. The residue was then fused with potassium pyrosulfate, and the titanium determined as above; 100 mg. of titanium oxide were found.

Finally, a given weight of pure potassium titanium fluoride containing 70 mg. of titanium oxide was taken, and evaporated twice to dryness with 20 cc. of hydrofluoric acid. When the residue was analyzed gravimetrically, 68.5 mg. of titanium oxide were found.

These tests show that while hydrofluoric acid alone may have a tendency to volatilize titanium, the effect is so slight, even on pure, freshly precipitated material, that it would be useless as a method of eliminating titanium for the purpose of preventing its interference in the persulfate color method.

It is recommended that potassium periodate be used as the oxidizing agent in the presence of much titanium. Sodium bismuthate can also be used successfully, as there is no interference with the development of the manganese color.

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Determination of Selenium in Organic Matter

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In 1934 Robinson, Dudley, Williams, and Byers (*2*) published a series of methods for accurate estimation of small quantities of selenium, which included a modification suggested by Van Kleeck for vegetation. This modification has been found generally satisfactory and perhaps the best hitherto available. Several thousand determinations have been made by its use (*1*). The method provides for the preparation of the sample by digestion with concentrated sulfuric acid as in the Kjeldahl method for nitrogen and subsequent distillation with concentrated hydrobromic acid and bromine. There are two unsatisfactory features in this procedure: In order to estimate quantities of selenium as low as 1 to 2 parts per million it is necessary to digest 10 grams of the air-dry vegetation, and even with the aid of mercuric oxide as a catalyzer this requires 6 to 8 hours for completion. Also, unless the digestion is carefully regulated the evolution of gases—carbon dioxide, sulfur dioxide, and water vapor—is so rapid that there is danger of loss of small quantities of selenium which are not absorbed by the bromine trap. The modification described below has been found to be much more rapid in execution, lends itself to routine work more readily, and is, when properly executed, free from all danger of selenium loss.

To prepare a sample of air-dry vegetation it is first ground to pass a 2-mm. mesh sieve, then mixed and quartered. A weighed sample, usually 10 grams, is stirred into a mixture of 50 cc. of concentrated sulfuric acid and 100 cc. of nitric acid in a 600-cc. Pyrex beaker. The mixture is stirred with a thermometer until it becomes homogeneous, after the first few minutes with gentle heating, without allowing the temperature to rise above 100° C. After all frothing has ceased, the temperature of the mixture is raised to a maximum of 120° C. until all evolution of nitrogen peroxide has ceased. The end of the operation is marked also by an incipient carbonization of the mixture, although longer heating at or below 120° C. does little harm. After the mixture is cooled it is transferred to an all-glass distilling flask, 100 cc. of hydrobromic acid and 1 cc. of bromine are added, and 75 cc. of distillate are collected. Care is taken that the first portion of the distillate contains a small excess of bromine.

Table I. Selenium Content of Vegetation as Determined by Kjeldahl and Wet-Combustion Procedures

Lab. No.	Material	Selenium Content: Kjeldahl digestion	Selenium Content: Wet combustion
		P. p. m.	*P. p. m.*
B14447	Astragalus grayii	1200	1280
		1180	1260
14448	Mixed vegetation	12	15
		12	15
		14	
14481	Corn	3	5
		2	5
14482	Corn	10	10
		7	10
14796A	Tium racemosum	450	460
14853	Stanleya bipinnata	460	530
14733A	Tium racemosum	45	70
14718A	Tium racemosum	150	160
16187	Diholcos bisulcatus	370	550
16190	Vegetation, not identified	7	18
16193	Sunflower	3	7
16197	Wild aster	220	310
16199	Corn	4	4

The further procedure—filtration to remove wax, precipitation with sulfur dioxide and hydroxylamine hydrochloride, and subsequent estimation by color or weighing—is as previously described. The only important precaution to be observed is to remove the nitric acid, completely, by digestion. If this is not done the distillate will contain nitroxyl tribromide, which is not decolorized by sulfur dioxide and requires excessive quantities of hydroxylamine hydrochloride. If the temperature be allowed to rise until fumes of sulfur trioxide are evolved, certain loss of selenium will ensue. In Table I are given the results obtained upon identical samples by the procedure suggested and by the Kjeldahl digestion.

TABLE II. SELENIUM CONTENT OF VEGETATION

(Comparison by treatment with nitric and sulfuric acids to incipient carbonization after removal of nitric acid at 120° C. and by subsequent heating for half an hour.)

Lab. No.	Material	Selenium Content by Wet Combustion Method: Incipient carbonization	Selenium Content by Wet Combustion Method: Heated 0.5 hr. after carbonization
		P. p. m.	*P. p. m.*
B15942	Wheat grass	10	5
15944	Side oats grama	2	2
15946	Wild aster	210	195
15948	Wild aster	8	6
15950	Little blue stem	1	1

In Table II are given five determinations made by wet digestion heated to incipient carbonization and for half an hour after carbonization has occurred but without allowing the temperature to rise above 120° C. It will be observed that while a rather minor loss of selenium is produced by heating beyond carbonization, such practice is inadvisable.

By contrast when standard sample B14447, Table I, was heated with nitric and sulfuric acid until white fumes of sulfur trioxide were evolved, the quantities of selenium found were, in two samples, 770 and 710 parts per million. It is therefore essential that during the wet-combustion process the temperature be kept low.

Small as is the modification suggested, it is of importance if large numbers of determinations are to be made, since the time required to prepare a sample for distillation is but 2 hours as against 6 to 8 for the Kjeldahl digestion. It is also more accurate, particularly for large quantities of selenium. By the use of this procedure an experienced operator with suitable equipment may readily effect distillation of twenty-four samples in an 8-hour day.

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RECEIVED September 2, 1935.

Quantitative Analysis of Solutions by Spectrographic Means

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A method for determining the amounts of metallic elements in a solution of their salts is described. An uncondensed spark in air between a suitably chosen solid electrode and the solution under analysis is photographed, and, from measurements on the relative intensities of chosen spectral lines, the analysis is made by reference to previously determined working curves. An internal standard is employed. Two methods for correcting for the influence of the presence, in varying amounts, of one element on the intensity of the spectral lines of another are described. The method has been applied in the determination of sodium, potassium, magnesium, and calcium in solutions of mixtures of their salts in concentrations varying over the range of their occurrence in human urine. The accuracy of analysis of an unknown is, in general, such as to give an error of about 2 per cent of the amount of the test element present.

METHODS for quantitative analysis by spectroscopic means have been developed to such a degree of reliability that it seemed desirable to investigate the feasibility of applying them to the determination of the inorganic bases in biological materials. The Department of Internal Medicine of the university became interested in the problem and it has been carried out as a joint investigation by this department and the Department of Physics. In this paper, the general technic for making quantitative analyses for metallic elements in a mixture of their salts will be described. The fundamental method employed is the same as that described by Duffendack, Wolfe, and Smith (*1*), except that a different spectroscopic source was demanded.

The particular problem that had to be solved was that of making correct determinations of the several metallic elements in the presence of each other when the amounts of the elements present in different solutions of the same salts varied over considerable ranges. As the presence of one element or ion oftentimes markedly affects the intensities of the spectral lines of another, corrections had to be found for such of these effects as appeared. Two methods were devised for making corrections for the effect of variations in the abundance of one element on the analysis for another. The technic has been worked out for the determination of sodium, potassium, magnesium, and calcium in solutions of mixtures of their salts over the ranges of abundance in which these elements occur in urine.

Spectroscopic Source

A number of spectroscopic sources were tested before one satisfactory for the purpose was found. It is essential that the solution under test be vaporized in such a way that the vapor shall contain the elements in amounts representative of their concentration in the solution. Hence the vaporization of the solution must not change the nature of the solution not yet used, and the solution must be fed into the spectroscopic source continuously, any part of it not volatilized being immediately removed.

The source found to be most satisfactory is an uncondensed spark in air between a suitable solid electrode and an electrode consisting of the solution itself. The material of the solid electrode should be one that permits ready and complete cleaning and has no spectral lines close to those used for the analyses. Silver was used in the present investigation. The solution is volatilized by the electric discharge.

The sparking apparatus, Figure 1, is a modification of one described by Twyman and Hitchen (*3*). *S* is the solid electrode. The solution is fed from the reservoir, *R*, through a capillary, *C*,

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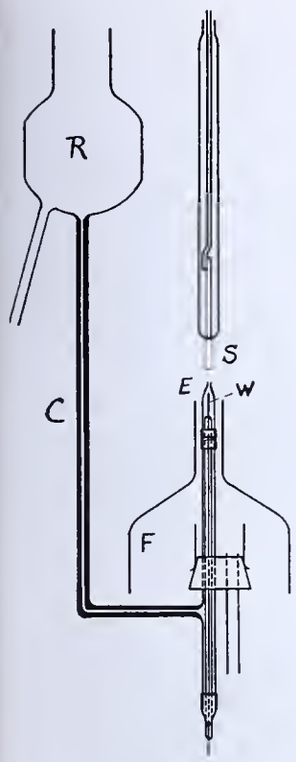

FIGURE 1. SPARK GAP FOR SOLUTIONS

into the electrode, *E*. The capillary regulates the rate of flow, which must be sufficiently rapid so that a considerable excess of the solution overflows into the waste receiver and only a small percentage is volatilized by the discharge. A flow of 2 cc. per minute was found to be satisfactory for the source employed. Electrical contact with the liquid electrode is afforded by a platinum wire, *W*, introduced into the electrode from below and kept 2 or 3 mm. below the surface, so that the spark does not pass directly to the wire.

A draft of air around the spark prevents the reëntry of any spray or vapor into the spark. This draft was achieved by blowing compressed air from a glass nozzle up through a funnel, *F*, surrounding the liquid electrode. The rate of flow of air can be easily regulated in practice by means of a water manometer.

The electrical connections for the spark are shown in Figure 2. The spark gap, *G*, was 11 mm. in length. The spark employed was excited by a 1-kva. 25,000-volt transformer, *T*, supplied with 110-volt 60-cycle current and regulated by means of the water-cooled rheostat, *R*. The ammeter, *P*, and the milliammeter, *S*, measured the primary and secondary currents, respectively. The secondary current was 32 milliamperes. A high-frequency spark generated by a Hartley oscillating circuit was also satisfactory.

The chief precautions to be observed with the source in order to obtain consistent analyses are to maintain constant the rate of flow of the solution, the strength of the air draft, and the amount of the spark current. A screen was interposed between the source and the split of the spectrograph in such a manner that light from only the lower half of the spark entered the spectrograph. A deposition of material from the solution was observed to accumulate on the upper electrode and the spectral lines of this material appeared in the portion of the spark adjacent to this electrode. As it was found that all of the materials in the solution are not proportionately represented by their spectral lines from this deposited material, it is better to avoid the use of this portion of the spark.

Fixing Excitation Conditions

The complete development of the method of analysis consists of three parts, (*a*) fixing the excitation conditions, (*b*) determining the working curves, and (*c*) analyzing the unknown specimen. These steps are in every way analogous to those of the method of Duffendack, Wolfe, and Smith (*1*), and obviously steps *a* and *b* need be done only once for a given kind of solution.

After the lines to be used for the analysis are definitely selected, the variation of the relative intensities of these lines with changes in the spark current and other factors in the source should be investigated and those conditions of excitation chosen that are easily maintained practically constant. The conditions should be such that small variations in them, especially the spark current, do not produce appreciable variations in the relative intensities of the selected lines. It is important also that the spectrum be excited without any background.

SELECTION OF SPECTRAL LINES. Many factors require consideration in the selection of the spectral lines. Sometimes, of course, one is limited, as in this case, to the very few lines that appear in the spectrum of the material to be analyzed, but oftentimes more lines can be brought out by changing the excitation conditions and usually there is considerable choice of lines. With a spark source, it is safer to use only arc lines or only spark lines for the analysis and not compare arc and spark lines, as the relative intensities of lines of such radically different classes may vary rapidly with changes in the excitation conditions. For the case under consideration, only arc lines were used, and the spark was operated so as to be as arc-like as possible. The lines to be compared should lie close together in the spectrum, and, if a number of elements are to be estimated from a single spectrogram, all the selected lines, including those of the standard, should lie in a region of constant contrast of the photographic plate. For the solutions described above, the following lines, or unresolved multiplets, were selected: sodium 3302 Å., potassium 4046 Å., magnesium 2852 Å., and calcium 4226 Å. Cadmium was used as the internal standard and its lines at 3261 Å., 3466 Å., and 3610 Å. were chosen for comparison. All these lines were separated far enough from other lines and the water vapor bands so that their densities could be accurately measured. Their relative intensities were determined by the method of Thomson and Duffendack (*2*).

Determination of Working Curves

The basic principle of this method of analysis is that the relative intensities of spectral lines emitted by different elements in a spectroscopic source are determined by functions of their relative abundance. Then, if some element, the standard, is present in known concentration, the concentrations of the other elements can be determined if the correct functions can be discovered. These functions are determined empirically by a set of control measurements on solutions made up synthetically and, hence, of known composition. These functions plotted graphically constitute the working curves for the analysis of the unknowns. For convenience, the logarithms of the relative intensities of lines of a test element and of the standard are plotted against the percentage of the test element in the solution, as shown in Figure 3.

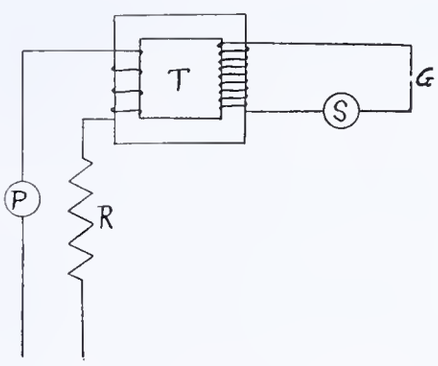

FIGURE 2. ELECTRIC CIRCUIT

Unfortunately, the relative intensity of a line of a test element with respect to a line of the standard may vary with the concentration of another element in the solution. When the disturbing element varies in concentration, corrections have to be made for its effects on the analysis of the test element. Methods for making these corrections to the working curves are described below. Working curves and corrections for the effects of the several metals on the analyses of one another have been determined for mixtures of the salts of sodium, potassium, magnesium, and calcium with cadmium as the internal standard over the following ranges of percentage composition: sodium 0.1 to 1.2 per cent, potassium 0.1 to 1.2 per cent, magnesium 0.0025 to 0.015 per cent, and calcium 0.04 to 0.15 per cent. The cadmium was maintained at a known concentration.

EFFECT OF PRESENCE OF ONE ELEMENT ON ANALYSIS FOR ANOTHER. The effect of one element on the determination of another arises from several causes, which may be separated into two groups—changes in the characteristics of the solution, and changes in the nature of the vapor and in the interactions

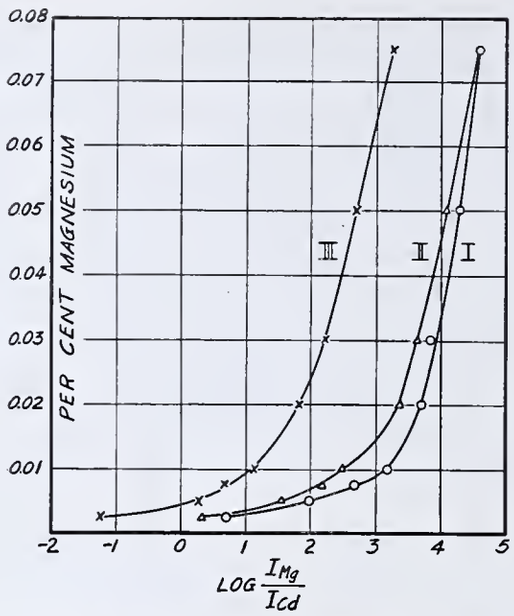

FIGURE 3. WORKING CURVES FOR ESTIMATION OF MAGNESIUM

I. Mg 2852 Å., Cd 3261 Å.
II. Mg 2852 Å., Cd 3466 Å.
III. Mg 2852 Å., Cd 3610 Å.

within the vapor. Variations in the amount of one of the salts of the solution may be expected to alter the electrical conductivity and volatility of the solution. If the volatility of the solution is changed, the character of the vapor, its density, its composition, and its electrical conductivity will likewise change.

In the vapor excited by the electric spark, interactions between the elements may be expected to occur, especially in impacts of the second kind between the excited atoms or ions of one kind and normal atoms of another. Such interactions markedly affect the intensities of the spectral lines of the reacting elements, and so must be discovered and allowed for in the results. These impacts are most probable between atoms which have energy states in close resonance with each other and affect the intensities of the lines originating in these states much more than other lines in the spectrum. If possible, it is best to avoid using lines originating in such states.

Not only do the positive ions affect the relative intensities of the spectral lines of each other, but effects were observed from the negative ions as well. The chloride ion was found to enhance the intensities of all the lines without, however, appreciably changing their relative intensities. The sulfate and phosphate ions, on the other hand, were observed to decrease the relative intensities of the lines of all the elements in the solutions used with respect to the lines of cadmium. The phosphate ion has a greater effect in this way than the sulfate ion. On account of these effects, it is necessary for accurate determinations first to convert all the salts to a single acid radical by appropriate chemical processes.

Method of Excess

In the case of the solutions tested, sodium, potassium, and magnesium were each found to decrease the relative intensity of the spectral line of each of the other elements with respect to those of cadmium. Calcium slightly increased the relative intensities of the lines of potassium and magnesium with respect to those of cadmium, but decreased that of sodium. Investigation revealed that the amount of the effect increased with an increase in the concentration of the disturbing element or elements, but reached an approximately constant value at relatively high concentrations. An example of this effect is given in Figure 4, which shows the change in the intensity of the calcium line relative to the cadmium lines brought about by increasing the concentration of sodium in the solution. The effect approaches a constant maximum value.

The observation that the disturbing effect of an element approached a constant maximum value led to the development of the method of excess for eliminating errors in analysis due to such disturbing effects. By separating the unknown solution to be analyzed into four portions and adding to that portion of the solution under test for sodium, for example, excess amounts of the disturbing elements, so that small variations in their concentrations in the original solution no longer produced variations in the determination of sodium, the concentration of sodium in the unknown could be accurately determined. The other portions of the solution were similarly treated with excess amounts of the elements which disturbed the determination of the metal under test, and so the original solution could be completely analyzed. This method obviously demands a larger amount of the original solution for analysis than one in which all of these elements are determined from a single spectrogram.

It was observed in the use of the method of excess that sometimes an excess of one of the disturbing elements reduced the amount of another disturbing element that must be added to eliminate the variations of its disturbing effect. Thus, in the analysis of the solution discussed above, the addition of 1 per cent of sodium and 1 per cent of potassium rendered the disturbing effects of both the elements on the determination of magnesium constant, whereas 2 per cent of either alone was required to eliminate variations due to the single element.

The analysis of solutions of mixtures of the salts used as an illustration in this paper was accomplished by the method of excess as follows:

For the determination of magnesium, there were added to a portion of the unknown 2 per cent of cadmium for internal standard and 1 per cent of sodium, 1 per cent of potassium, and 0.5 per cent of calcium.

For the determination of sodium, there were added to another portion of the unknown 1.5 per cent of cadmium for internal standard and 2 per cent of potassium, 0.25 per cent of magnesium, and 0.25 per cent of calcium.

For the determination of potassium, there were added to a third portion of the unknown 1 per cent of cadmium for internal standard and 2 per cent of sodium, 0.25 per cent of magnesium, and 0.25 per cent of calcium.

For the determination of calcium, there were added to a fourth portion of the unknown 0.5 per cent of cadmium for internal

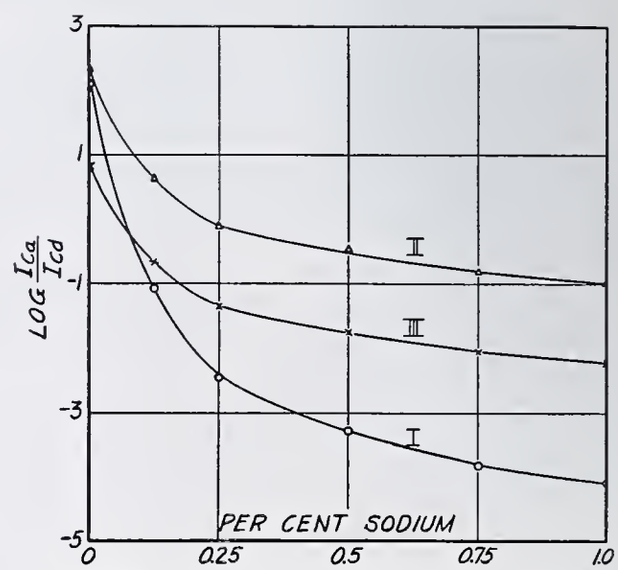

FIGURE 4. EFFECT OF SODIUM ON RELATIVE INTENSITIES OF CALCIUM AND CADMIUM LINES

I. Ca 4226 Å., Cd 3261 Å.
II. Ca 4226 Å., Cd 3466 Å.
III. Ca 4226 Å., Cd 3610 Å.

Table I. Analyses of Solutions by Method of Successive Approximations

Sodium				Potassium				Magnesium				
Spectrographic			Actual	Spectrographic			Actual	Spectrographic				Actual
%			%	%			%	%				%
0.198,	0.198,	0.214	0.200	0.207,	0.200,	0.206	0.200			0.0076,	0.0076	0.0075
0.408,	0.394,	0.404	0.400	0.408,	0.393,	0.386	0.400		0.0097,	0.0098,	0.0099	0.010
0.594,	0.581,	0.588	0.600	0.612,	0.603,	0.592	0.600	0.0147,	0.0157,	0.0154,	0.0156	0.0155
0.753,	0.762,	0.749	0.800	0.784,	0.790,	0.759	0.800			0.0199,	0.0203	0.020
0.993,	0.988,	0.983	1.000	0.946,	0.932,	0.905	1.000		0.0311,	0.0293,	0.0295	0.030

standard and 2 per cent of sodium, 2 per cent of potassium, and 0.25 per cent of magnesium.

The chlorides of the metals were used in all cases and the solution was acidified by adding 2.5 cc. of concentrated hydrochloric acid per 100 cc. of solution.

The average errors in analyzing by this method a number of synthetic solutions, of composition unknown to the analyst, in which the test elements varied over the ranges given above were: for magnesium 1.9 per cent and for sodium 1.2 per cent of the amounts of these elements present. The maximum errors were 2.8 and 2.0 per cent, respectively. The method of excess was found to be not so accurate for the determination of potassium and of calcium. In the latter case the average error was about 5 per cent. The lack of accuracy with these two elements was due to the development of a continuous background in the region of the potassium and calcium lines when an excess of sodium was added to the solution. Furthermore the excess of potassium necessary for the calcium determination produced a marked weakening of the calcium line and consequent difficulty in the measurement of its intensity relative to that of the standard cadmium line.

Method of Successive Approximations

Since the use of excessive quantities of interfering elements did not give sufficiently accurate determinations for potassium and calcium, and since this method requires that each element be determined separately, other methods for correcting for the effect of the elements on each other were sought. One method which involves the use of successive approximations was found satisfactory. The solutions used in establishing the working curves were made up so that the curves might be used for the analysis of urine directly.

These solutions were made by adding the desired amount of each element in the form of a rather concentrated solution of the chloride salt (chlorides being used owing to the insolubility of calcium sulfate) to a volumetric flask. To this mixture were then added sufficient hydrochloric and sulfuric acids so that after dilution the total concentration of the chloride ion would be 0.5 N and the concentration of the sulfate ion would be 0.5 N plus the sum of the hydrogen equivalents of the bases present. Sufficient cadmium chloride solution was then added so that the concentration of cadmium in the final volume would be 1.5 per cent, and the solution was diluted to volume. Thus to use the curves obtained with these solutions for urinary analyses it would be necessary to remove the phosphates from the urine, ash the filtrate with sulfuric acid until the excess acid was removed, dissolve the ash with 10 cc. of 5 N hydrochloric acid or its equivalent, add to this solution 5 cc. of 10 N sulfuric acid, and 10 cc. of a solution of cadmium chloride containing 15 per cent of cadmium, and dilute to 100 cc.

It was found that, in the quantities present, sodium and potassium had the predominant effects on the analyses. Thus, by this method, it was necessary to correct the sodium determinations for the presence of potassium only and vice versa. The magnesium estimations had to be corrected for both sodium and potassium. Calcium occurs in such small quantities in the urine that the authors have not been able as yet to get sufficiently accurate determinations of its concentration in synthetic solutions in its normal range of occurrence in urine.

Sodium and potassium may be estimated in the following manner: Working curves for each element are determined in the presence of the internal standard element and of the acids only. For a number of concentrations of each element, the relative intensities of the selected pairs of spectral lines, one of the element in question and the other of the internal standard element, are determined with varying concentrations of the interfering element. These relative intensities are then set up in table form for each of the elements. The analysis of a solution of unknown composition for sodium and potassium is then carried out as follows:

From the working curves, a first approximation of the concentration of each element present can be determined. Using the concentration, so determined, of each element as the concentration of the interfering element, a second approximation may be obtained for the concentration of each, by the use of their respective correction tables. This procedure is continued until the desired degree of precision is obtained. Usually the third approximation has been found sufficient.

After the concentrations of sodium and of potassium have been determined, that of magnesium may be obtained. Since the effects of sodium and of potassium on the relative intensity of the spectral lines of magnesium and of cadmium are almost equal for equal concentrations, this process is relatively simple. A table was prepared of the relative intensities of the magnesium and cadmium lines for several concentrations of magnesium and varying concentrations of sodium and potassium. The headings of the columns give the total concentration of sodium and potassium; under each are three subcolumns for ratios of sodium to potassium of 1 to 3, 1 to 1, 3 to 1. Thus after the concentrations of sodium and of potassium have been found, the experimentally determined ratio of the intensities of the spectral lines of magnesium and of cadmium may be applied to the proper column in the table and by interpolation the amount of magnesium can be obtained.

In Table I are given the representative precision and accuracy of the analyses of solutions of the class described above for sodium, potassium, and magnesium. Each spectrographic value was obtained from a single spectrum.

The errors in the analyses of unknowns of the character described by the method of successive approximations are, on the average, for sodium 2 per cent, for potassium 3 per cent, and for magnesium 2 per cent of the amounts of these elements present.

Acknowledgment

The writers wish to express their gratitude for a grant-in-aid from The Faculty Research Fund of the University of Michigan which enabled them to carry out this investigation.

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Determination of True Free Sulfur in Vulcanized Rubber

A Modification of the Thiocyanate Method

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For the determination of true free sulfur in vulcanized rubber a method has been proposed by Davis and Foucar, whereby the acetone extract of the original sample is treated with boiling alcohol and a small lump of potassium cyanide to convert the free sulfur into potassium thiocyanate and the latter titrated with a standard solution of silver nitrate. The application of this method, however, always meets with difficulty due to an excess of cyanide going into solution together with the thiocyanate formed, rendering the end point of the final titration indistinct. In this paper are given the results of experiments which were carried out by the present authors to overcome this difficulty through the successful separation of cyanide from thiocyanate by their difference of solubility in acetone.

IT IS WELL known that the acetone extract of vulcanized rubber contains not only free sulfur, but in some cases also certain sulfur compounds which can be converted into sulfate by oxidation. Davis and Foucar (*2*) proposed a method to determine the true free sulfur contained in acetone extract of vulcanized rubber, as follows:

> The sample of the rubber stock is extracted by acetone as usual, the acetone is driven off from the extract, and the dried mass is heated under a reflux condenser with alcohol and a small lump of potassium cyanide. The free sulfur contained in the extract is converted into potassium thiocyanate. The solid cyanide remaining is removed, and alcohol is driven off by evaporation. The residue is treated with water, and a slight excess of nitric acid and some iron alum are added. The characteristic blood-red coloration of ferric thiocyanate appears. Titration is then carried out with a standard solution of silver nitrate until the red color disappears.

In applying this method, however, difficulty was always found in that some of the potassium cyanide used for the conversion of free sulfur into the form of thiocyanate goes into solution, rendering the end point of the final titration indistinct. To eliminate this difficulty, a modification was proposed by Castiglioni (*1*), consisting of shaking the mixture of cyanide and thiocyanate with a 20 per cent solution of formaldehyde to convert the cyanide into glycolic acid and hexamethylene tetramine, neither of which is considered to have any influence upon the final titration.

The present authors, however, found that there was much left to be desired in Castiglioni's method, because sufficient cyanide always remained unreacted to render the end point of the titration indistinct, and they were led to the idea that it is better to eliminate the cyanide completely by the use of a suitable solvent. Acetone was found eminently suitable for this purpose. It does not dissolve potassium cyanide to any appreciable extent, but at 22° C. dissolves 17.2 per cent of its weight of potassium thiocyanate (*3*).

To determine the suitability of acetone for this purpose, the following preliminary experiments were carried out:

1. Test for the insolubility of potassium cyanide in acetone.
2. Test for the limit of amount of cyanide influencing the end point of the titration of thiocyanate by silver nitrate solution.
3. Test for the separation of cyanide from thiocyanate by means of acetone.

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Preliminary Experiments

TEST FOR THE INSOLUBILITY OF CYANIDE IN ACETONE. Various quantities of an alcoholic solution containing 0.00048 gram of potassium cyanide per cc. were accurately measured into flasks. The alcohol was distilled off and each residue digested with 20 cc. of acetone by gentle warming on the water bath under the reflux condenser for 30 minutes. After complete cooling, the acetone was filtered through a filter paper as quickly as possible and the filter washed several times with cold acetone. The cyanide on the filter and that adhering to the inside wall of the flask were dissolved with water, the solutions united, and then titrated with 0.01 *N* silver nitrate, with a few drops of 10 per cent solution of potassium iodide as indicator.

For comparison, the experiments were also carried out with the original alcoholic solution of cyanide without digestion with acetone. The results are shown in Table I.

TABLE I. ANALYSIS OF POTASSIUM CYANIDE BEFORE AND AFTER DIGESTION WITH ACETONE

No.	KCN Alcoholic Solution Taken	KCN in Alcoholic Solution Taken	0.01*N* $AgNO_3$ Solution Used	KCN Found
	Cc.	*Gram*	*Cc.*	*Gram*
1 Digested with acetone	5.0	0.0024	3.6	0.0023
2 Digested with acetone	10.0	0.0048	7.1	0.0046
3 Digested with acetone	20.0	0.0096	14.1	0.0091
4 Not digested with acetone	10.0	0.0048	7.3	0.0047
5 Not digested with acetone	20.0	0.0096	14.6	0.0094

The differences between the results for samples 2 and 3 which were digested with acetone and 4 and 5 which were not, are so slight that they may be regarded as within the limit of experimental error.

TEST FOR THE LIMIT OF AMOUNT OF CYANIDE INFLUENCING THE END POINT OF THE TITRATION OF THIOCYANATE WITH THE SOLUTION OF SILVER NITRATE. Several 5-cc. portions of a 0.107 *N* aqueous solution of purified potassium thiocyanate were accurately measured into conical flasks, to which various amounts of a 0.1016 *N* aqueous solution of potassium cyanide were added. The contents of the flasks were diluted with water up to about 25 cc. and acidified with a few cubic centimeters of 30 per cent nitric acid. Titration was carried out with a 0.05 *N* solution of silver nitrate, using a 5 per cent solution of ferric nitrate as indicator. The results are shown in Table II.

The results in Table II show that no influence appeared until the content of cyanide reaches to the amount of experiment No. 6 or about 0.0005 mole of potassium cyanide in about 35 cc. of solution at the end of the final titration. Indistinctness of the end point was always observed when the concentration of cyanide exceeded this limit, increasing as the concentration of cyanide increased.

Table II. Influence of Potassium Cyanide upon the Titration of Potassium Thiocyanate with Silver Nitrate Solution

No.	0.107*N* KCNS Solution Taken	0.1016*N* KCN Solution Added	KCN in Solution Added	0.05*N* $AgNO_3$ Solution Used	End Point
	Cc.	*Cc.*	*Gram*	*Cc.*	
1	5.0	0	0	10.7	Distinct
2	5.0	1.0	0.0066	10.6	Distinct
3	5.0	2.0	0.0132	10.6	Distinct
4	5.0	3.0	0.0198	10.6	Distinct
5	5.0	4.0	0.0264	10.5	Distinct
6	5.0	5.0	0.0330	10.8	Somewhat indistinct
7	5.0	10.0	0.0660	10.8	Somewhat indistinct
8	5.0	15.0	0.0990	10.8	Somewhat indistinct

Table III. Titrating Thiocyanate with Silver Nitrate after Separating Cyanide by Means of Acetone

No.	0.0996*N* KCNS Alcoholic Solution Taken	Solid KCN Added	0.05*N* $AgNO_3$ Solution Used	End Point
	Cc.	*Gram*	*Cc.*	
1	10.0	0	19.9	Distinct
2	10.0	About 1	19.8	Distinct
3	10.0	About 1	19.9	Distinct

Table IV. Comparison, through Estimation of Pure Sulfur, of Results Obtained by Modified and Oxidation Methods

Method Used	Sample of Sulfur Taken	Time of Boiling with KCN	$BaSO_4$ Found	Sulfur Found
	Gram	*Min.*	*Gram*	%
New modified method	0.0100	30	....	99.4
	0.0100	40	....	99.4
	0.0100	60	....	99.4
Oxidation method	0.0100	..	0.0727	99.9
	0.0158	..	0.1149	99.9

Test for the Separation of Cyanide from Thiocyanate by Means of Acetone. Ten cubic centimeters of a 0.0996 *N* alcoholic solution of purified potassium thiocyanate were accurately measured into a 100-cc. flask and diluted with alcohol up to about 50 cc. To this solution was added about 1 gram of potassium cyanide and the flask was heated under a reflux condenser for half an hour. The solution was evaporated to dryness, 30 cc. of acetone were added to the residue and the flask was shaken for a few minutes, while being gently warmed. On cooling, the contents of the flask were quickly filtered and washed several times with acetone. The filtrate was received in a 300-cc. flask and the acetone distilled off. The residue in the flask was dissolved in water, and 5 cc. of 30 per cent nitric acid were added. Titration was carried out with 0.05 *N* solution of silver nitrate, with 5 per cent solution of ferric nitrate as indicator. The results are shown in Table III.

These results show that acetone is a suitable solvent for removing cyanide and giving a distinct end point to the titration of thiocyanate with the solution of silver nitrate. From this fact, the method proposed by Davis and Foucar may be successfully modified and the difficulty of indistinct end point eliminated.

Procedure of Modified Method

Heat the dried acetone extract of vulcanized rubber for half an hour with 25 cc. of absolute alcohol and a small lump of potassium cyanide under a reflux condenser on a water bath, distill off the solvent, shake the dried mass with about 30 cc. of acetone for a few minutes, remove the undissolved residue by filtration, and wash with acetone. After evaporating the filtrate on the water bath, dissolve the dried substance with 50 cc. of water, add 5 cc. of 30 per cent nitric acid and a few drops of 5 per cent solution of ferric nitrate; shake the solution vigorously, and titrate with 0.1 *N* solution of silver nitrate until the blood-red coloration of ferric thiocyanate has disappeared.

Calculate the free sulfur content in original rubber sample as follows:

$$\text{Percentage of free sulfur} = \frac{0.003206 \times \text{cc. of } 0.1\,N\ AgNO_3 \text{ solution used for titration}}{\text{weight of sample (grams)}} \times 100$$

Application of Modified Method

Analysis of Pure Sulfur. To test the accuracy of the modified method, it was applied to the estimation of sulfur purified by means of sublimation in a glass retort, the purified sulfur being monoclinic crystal with a melting point of 119.0°–119.2° C. and leaving no trace of ash when incinerated. The results were also compared with those obtained by the ordinary oxidation method whereby the sample is oxidized into sulfate by means of bromine and fuming nitric acid. The results obtained by the two methods are almost concordant with each other, as shown in Table IV.

Analysis of Rubber Stocks. For exemplifying the application of the modified method, the rubber compounds given in Table V were prepared, and the ordinary oxidation method was also applied to the same samples for comparison. The results are shown in Table VI.

Table VI indicates that samples 1 and 3 give the same results by both methods within the limit of experimental error; on the other hand, sample 2 gives somewhat higher results by the oxidation method than by the modified method. This is probably due to the fact that the acetone extract of sample 2 contains an undervulcanized portion of the incorporated brown substitute containing some combined sulfur which can be oxidized to sulfate.

Applications were also made for the analysis of rubber insulation of a flexible joint wire manufactured by a Japanese cable maker, and a stamp mat employed in the post office. The results are shown in Table VII.

For the rubber insulation, the results of both methods are very close. For the stamp mat, however, the difference in results is rather remarkable.

Summary

The limit of quantity of potassium cyanide was determined as regards the interference with the end point of the titration of potassium thiocyanate with silver nitrate solution.

Acetone was found to be a suitable solvent for the separation of potassium cyanide from potassium thiocyanate.

Table V. Composition of Rubber Stocks for Analysis

No.	Composition: Standard smoked sheet	Zinc oxide	Sulfur	D. P. G.	Brown substitute	Vulcanization: Steam pressure	Time
						Kg./sq. cm.	*Min.*
1	100	5	5	1	0	2.81	30
2	100	5	5	1	5	2.81	30
3	100	5	40	1	0	4.22	300

Table VI. Results of Analysis of Prepared Rubber Stocks

No.	Free Sulfur Found: New modified method	Oxidation method
	%	%
1	2.66	2.76
	2.66	2.77
2	1.17	1.30
	1.17	1.31
3	0.21	0.27
	0.21	0.28

Table VII. Analysis of Free Sulfur in Commercial Rubber Goods

Kind of Sample	Free Sulfur Found: New modified method	Oxidation method
	%	%
Rubber insulation	0.13	0.17
	0.13	..
Rubber stamp mat	1.01	1.20
	1.01	1.20

A new modified method was proposed for the determination of true free sulfur in vulcanized rubber, by the use of acetone to remove the cyanide which renders obscure the end point of the titration of thiocyanate with silver nitrate solution. The proposed method was applied to the analysis of pure sulfur and some rubber goods, and was ascertained to be accurate and easy to carry out, requiring no special apparatus.

Acknowledgment

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Determination of the Fineness of Nitrocellulose by Dye Absorption

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THE purification of nitrocellulose used in the manufacture of smokeless powder, lacquers, etc., customarily includes wet grinding in one or more types of beaters, for the purpose of mechanically liberating occluded acidity as well as reducing the particle size of the nitrocellulose. The control of the final particle size at the end of the beating process is of considerable importance in some cases.

When only one type of beater is used, practical control of the fineness may be obtained by the use of a simple settling test. However, different types of beaters have distinctly different actions. Any one type of beater may produce fibers of a type in which chopping, crimping, fibrillation, flattening, or crushing is the major action. Types of these fibers are shown in Figure 1. In addition, the type of fiber produced will vary according to whether wide or narrow blades are used in the beating engine. Because of this difference in beater effects, nitrocellulose subjected to beating in different types of machines may be of the same degree of fineness as judged by a settling test, but differ considerably in specific surface, which must be considered to be representative of true fineness.

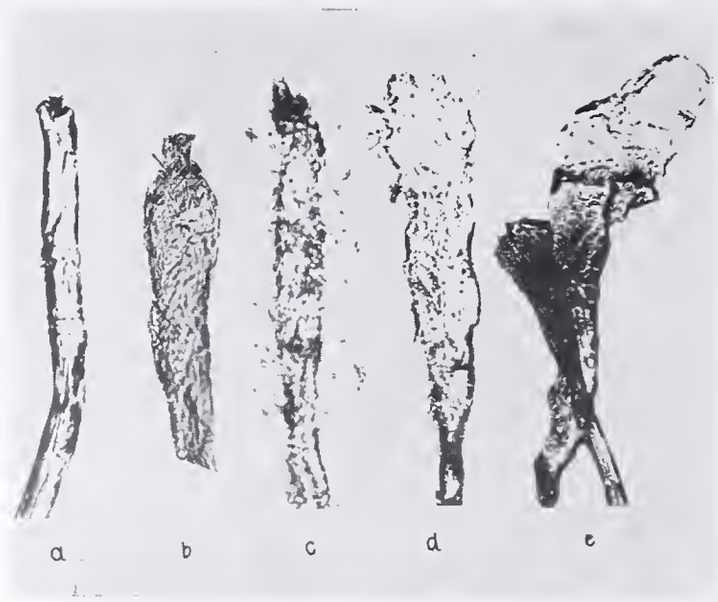

Figure 1. Types of Beaten Fibers

a, chopped; *b*, crimped; *c*, fibrillated; *d*, crushed; *e*, flattened

The specific surface is of importance with regard to the rate of purification in the boiling and poaching processes as well as in the rate of gelatinization by a solvent. It was therefore considered desirable to develop a test involving surface, in order that some numerical value might be given to the amount of specific surface produced, as beating progressed. Such a test would permit comparisons to be made between different types of beating engines and also furnish information with respect to the relation between consistency of pulp and type of beaten fiber obtained.

The method developed was the result of a large number of tests made to establish a relationship between increasing surface and increasing dye absorption. Tests by single dyeing, nonaqueous dyeing, and mordant dyeing methods were made, but no dye was found which did not penetrate the nitrocellulose and dye the fibers internally as well as externally. However, a satisfactory procedure was developed on the basis of the work of Pelet and Grand (*7*) and of Haller (*5*), who found that basic dyes may be quantitatively precipitated by acid dyes with the formation of weakly associated compounds.

If nitrocellulose fibers are dyed with either a basic or acid dye, washed, and treated with a dye of opposite sign, a definite amount of the latter is taken up as an insoluble precipitate on the surface of the dyed fibers. The amount of dye taken up should therefore be a measure of the specific surface.

Choice of Dyes

Since the excess of the first dye must be washed out of the fibers before the second dye is applied, it was thought that a choice might be made by dyeing nitrocellulose with different dyes, washing with water, and recording how many washes were necessary before a colorless filtrate was obtained. The dye or dyes which required the least washing would be most firmly fixed and thus tend to shorten the time required to carry out the complete process. These washing tests are recorded in Table I, and indicate that with regard to absence of bleeding Congo red, benzopurpurin, and acid violet negatively charged, and night blue positively charged, were superior to the rest.

The behavior of the dyes is in agreement with their molecular weights, the high molecular weight dyes being in the colloidal condition and tending to diffuse slowly. The low molecular weight compounds are designated as colloidal electrolytes and diffuse rapidly into or out of fibers.

Table I. Washing of Dyed Nitrocellulose

Dye	Mol. Wt.	Charge	No. of Washings	Remarks
New fuchsin	337	+	4	Still bleeding
Tartrazine	468	−	2	Completely removed from nitrocellulose
Chrysoidine	248	+	4	Still bleeding
Martius yellow	234	−	2	Completely removed from nitrocellulose
Acid violet	757	−	3	Colorless filtrate
Naphthol yellow	390	−	3	Completely removed from nitrocellulose
Benzopurpurin	724	−	3	Colorless filtrate
Alkali blue		−	2	Colorless filtrate
Methylene blue	319	+	4	Still bleeding
Congo red	696	−	3	Colorless filtrate
Malachite green	364	+	4	Still bleeding
Night blue	575	+	3	Colorless filtrate
Crystal violet	443	+	4	Colorless filtrate
Methyl violet	373	+	4	Still bleeding

The first dye chosen was the negatively charged Congo red, because of its peculiar behavior in dyeing cotton fibers. It has a greater affinity for the lumen than for the walls of the fiber and tends to concentrate at the center rather than at the surface of the hair. Bright (*3*) recommends Congo red for distinguishing between damaged and undamaged fibers because it penetrates the damaged portion and stains the lumen deeply. This was exactly the property desired, since the concentration of Congo red at the center tends to prevent the penetration of an oppositely charged dye to the same region.

A study of Knecht and Hibbert's (*6*) titration methods, using titanium trichloride, showed that some dyes required back-titration, some a boiling temperature, and others the addition of alcohol, sodium tartrate, Rochelle salt, etc., while methylene blue alone could be titrated directly at room temperature. In addition it was found that the bleeding of methylene blue, as shown in Table I, could be prevented by washing the dyed fibers with a buffer solution instead of pure water. Methylene blue was therefore chosen as the positively charged dye to be used.

Preparation of Dye and Buffer Solutions. For the dye solutions, 0.5 gram of Congo red or methylene blue was dissolved in 150 cc. of water, brought to a boil, cooled to room temperature, and centrifuged for 10 minutes at 1500 r. p. m. The supernatant liquid was decanted and made up to 500 cc. The methylene blue contained much insoluble matter and the solution was therefore less than 0.1 per cent in strength.

For the buffer solutions, 37.875 grams of powdered sodium tetraborate were made up to 1 liter in boiled distilled water, and

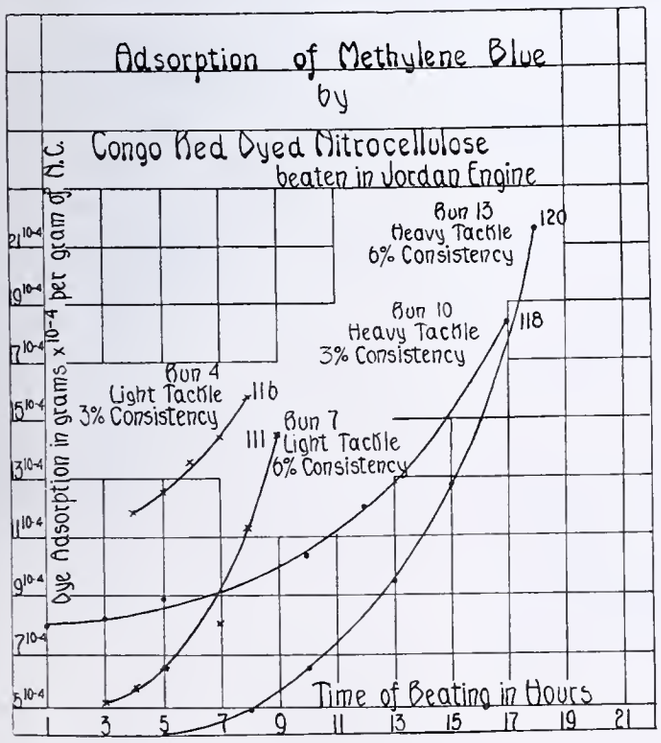

Figure 2

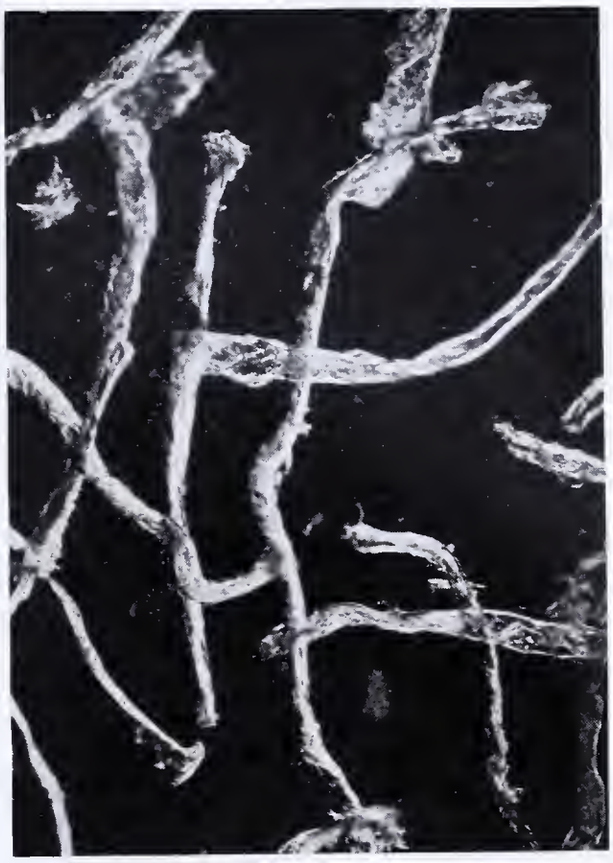

Figure 3. Photomicrograph of Run 4

Light tackle, 3 per cent consistency, 150 ×

10.9618 grams of granular c. p. sodium chloride and 46.515 grams of crystallized boric acid were dissolved in boiled distilled water and made up to 1 liter. Five cubic centimeters of the borax solution added to 5 cc. of the boric acid–sodium chloride solution gave a mixture having a pH of 7.9, as tested colorimetrically with LaMotte color standards, using phenol red as an indicator.

Ten grams of the mixed solution were evaporated to dryness in a glass capsule and dried for 2 hours at 140° C. From the weight obtained, the necessary dilution was made to secure a 3 per cent solution.

Standardization of Titanium Trichloride Solution. The standardization was carried out in an atmosphere of carbon dioxide, according to the method of Knecht and Hibbert (*6*). The following value was found:

$$1 \text{ cc. of } TiCl_2 = 0.001426 \text{ gram of methylene blue}$$

Experimental Procedure

Three grams of nitrocellulose were placed in a 250-cc. beaker containing 150 cc. of a borax–boric acid–sodium chloride buffer solution with a pH of 7.9 and a salt concentration of 3 per cent, soaked, and stirred until all the lumps are broken up. Five cubic centimeters of 0.1 per cent Congo red solution were added, the beaker was placed in a boiling water bath, and the contents were mechanically stirred and heated for exactly 15 minutes. The beaker was then removed from the bath and the contents were filtered through a platinum Gooch crucible. The nitrocellulose was removed from the crucible, placed in the beaker, and washed four times by decantation with 40-cc. portions of the buffer solution at 50° to 60°. A final 40-cc. portion was used to transfer the nitrocellulose back to the crucible and wash out the beaker. The crucible was sucked dry with vacuum, the contents were transferred to the original beaker, and 150 cc. of buffer solution added, a portion of the solution being used to clean out the platinum crucible. Then 12 to 15 cc. of 0.1 per cent methylene blue solution were added, heating and stirring carried out for 15 minutes, and the contents of the beaker filtered through the crucible, which was sucked dry. The filtrate was transferred to a 250-cc. flask, acidulated with 10 cc. of concentrated hydrochloric acid, saturated with carbon dioxide, and titrated with titanium trichloride solution. A blank without Congo red was run on the nitrocellulose and buffer solution.

FIGURE 4. PHOTOMICROGRAPH OF RUN 10
Heavy tackle, 3 per cent consistency, 150 ×

The amount of methylene blue absorbed on the Congo red dyed fibers was determined as follows:

Blank titration: 150 cc. of buffer solution boiled with 3 grams of nitrocellulose, filtered, 15 cc. of methylene blue solution added, and titrated with titanium trichloride.

0.011426 × cc. $TiCl_3$ (titration) = methylene blue in 15 cc. = A
$A/15$ = methylene blue in 1 cc. = B
B × cc. methylene blue added to unknown = total methylene blue = C
0.001426 × cc. $TiCl_3$ used for titrating excess methylene blue = D
$\frac{C - D}{3}$ = amount of methylene blue absorbed by 1 gram of nitrocellulose

Dyeing from Buffered Solutions

It has been pointed out by Birtwell, Clibbens, and Ridge (*2*) and by Bancroft (*1*), that dye absorption varies very markedly with the pH of the solution. Since nitrocellulose is beaten under conditions in which there may be absorption of either acid or alkali, the necessity for running the test in a solution of definite pH becomes apparent. Again, Congo red is negatively charged and consequently has but little affinity for nitrocellulose which is likewise negatively charged in water. But if a soluble inorganic cation is present, such as the sodium ion of sodium chloride, the positive charge of the sodium ion partially neutralizes the negative charge on the nitrocellulose, causing the negatively charged dye to be more readily absorbed and more firmly fixed. Finally with respect to evenness of dyeing, it was found that sodium chloride, sodium acetate, and sodium sulfate increased the depth of shade on the fibers without promoting evenness. Night blue was distinctly worse, with respect to evenness of dyeing, than methylene blue, crystal violet, or methyl violet. Six citric acid–sodium phosphate buffer solutions were prepared according to directions by Clark (*4*) having pH values of 2.1, 2.9, 4, 4.9, 6, and 6.8 and used in the dyeing tests. It was found that as the pH of the solutions changed from acid to neutral to alkaline conditions, the depth of color and uniformity increased up to a pH of 6. Above this figure there was no gain in evenness of dyeing while the depth of color continued to increase.

MICROSCOPIC EXAMINATION FOR EVENNESS OF DYEING. Examination of the fibers with a dark-field condenser was unsatisfactory, as the fibers usually appeared to be of a brilliant white color. Examination with reflected light in a metallurgical microscope showed no traces of color, but a black fiber. Transmitted light with the fibers air-mounted gave poor results and the best results were secured by immersion in a liquid of 1.52 refractive index. An 8-mm. objective was used with a 15 × eyepiece, the slide being oiled to the condenser with cedar oil.

FILTRATION AND WASHING OF DYED NITROCELLULOSE. In the first tests a porcelain Gooch crucible was used for filtration of the nitrocellulose after dyeing. It was found, however, that very finely divided nitrocellulose in a colloidal condition was being carried through into the filtrate and coagulated when the solution was acidified. A glass crucible with a porous, fritted glass bottom was tried but absorbed dye so strongly that it became necessary to wash it with acid after each filtration. In addition, it became choked with finely divided nitrocellulose and filtration was very slow. Recourse was made to a Munroe platinum Gooch crucible, as described by Snelling (*8*). This proved to be efficient and rapid.

Effect of Temperature

It was known from the literature that the best results in dyeing with Congo red were secured at boiling temperature, but conflicting statements were found as to what temperature was best for methylene blue. Accordingly, a series of tests at different temperatures was run with methylene blue in a buffered solution, the excess dye being titrated with titanium trichloride. The results follow:

Temperature	30°	50°	70°	80°	90°
$TiCl_3$ required for excess dye, cc.	2.4	2.2	1.5	1.1	0.7

This test indicates that under the same conditions with regard to concentration and pH of the solution, a larger amount of dye is deposited upon the fibers as the temperature of the dye solution is raised.

TABLE II. DYE ADSORPTION BY NITROCELLULOSE

Time of Beating *Hours*	Dye Adsorption, Grams × 10^{-4} per Gram of Nitrocellulose
Run 4, 3 per cent consistency, light tackle	
4	11.7
5	12.5
6	13.4
7	14.46
8	15.7
Run 10, 3 per cent consistency, heavy tackle	
1	7.85
3	8.20
5	8.90
10	10.35
12	11.92
17	18.28
Run 7, 6 per cent consistency, light tackle	
3	5.22
4	5.80
5	6.50
7	7.96
8	11.20
9	14.50
Run 13, 6 per cent consistency, heavy tackle	
5	4.10
7	4.92
10	6.62
13	9.35
15	12.78
18	21.40

Some experiments in removing the excess of Congo red from the dyed fibers showed that as many as 36 washings were necessary. If, however, the dyed material was washed with the buffer solution, five washings with a total of 200 cc.

were sufficient to remove the excess dye. It was also found that if the buffer solution was used at a temperature higher than that employed for dyeing, the dye would bleed from the cotton. A temperature of 95° C. for dyeing followed by washing with buffer solution at a temperature of 50° to 60° C. was finally adopted.

Relation between Surface and Dye Adsorption

The results of dye adsorption tests on nitrocellulose beaten in a Jordan engine are recorded in Table II and shown in the form of adsorption curves in Figure 2. Two consistencies or slurries were used, 3 and 6 per cent, and two sets of beating blades in the engine, narrow blades (light tackle) and wide blades (heavy tackle).

The fineness of each batch, as shown by settling tests in a 250-cc. graduated cylinder, is shown on Figure 2, the smaller the number the finer the material. Three of the samples showed approximately the same fineness—116, 118, and 120—but differed widely in their dye adsorptions. Microscopic examination of the 3 per cent consistency material, as shown in Figures 3 and 4, showed the reason for the difference in dye adsorption and indicated the superiority of such a test over the usual fineness test.

The difference in the development of specific surface for dye adsorption is due to the fact that when nitrocellulose is beaten, the pulp becomes thin and watery with the passage of time. The beating rolls cannot be set down rapidly and beating efficiency drops off. This is more noticeable with the thin than with the thick consistencies, which explains why a 6 per cent consistency as shown in run 13 develops a greater surface for dye adsorption than a 3 per cent consistency beaten for approximately the same length of time, as in run 10. The fineness test does not indicate this difference, the microscope discriminates but furnishes no quantitative information, while the dyeing test yields quantitative comparisons.

Summary

A double dyeing method for estimating the increase in specific surface of beaten nitrocellulose is described. The method involves dyeing the fibers with a negatively charged dye (Congo red) and the deposition of a positively charged dye (methylene blue) at and near the surface of the Congo red dyed fibers. Dyeing is carried out in a borax–sodium chloride–boric acid buffer solution of 3 per cent concentration, with a pH of 7.9, at 95° C. The dyeing tests, which were confirmed by microscopic analysis, indicate that products not only from different beaters but from the same beater may be differentiated. Such differentiation cannot be made by the standard fineness test.

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Application of the Spectrograph to the Determination of Carbon in Steel

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CHEMICAL analysis by the emission spectrum has been successful in the determination of the lesser metallic constituents of alloys. The extension of this method to the determination of small amounts of carbon would result in considerable saving in time, especially as against vacuum fusion methods.

To accomplish quantitative spectrographic analysis, the wanted element must be made to produce light in amounts which vary with the element's concentration. Before an element will emit light, its outer electrons must be raised to higher quantum states. As the charge on the nucleus increases from lithium's three to fluorine's nine, the number of electrons in the outer quantum level increases from one to seven; hence outer electrons in negative elements are enveloped by a more intense field than outer electrons in positive elements. It is therefore easier to force an electron farther away from its nucleus in elements like lithium and boron, than in elements like carbon and oxygen.

The problem of the spectrographic analysis of nonmetallic elements in the presence of metallic elements is one of putting enough potential into the arc or spark flame to excite atoms having their outer shells subjected to powerful nuclear fields. The difficulty is further increased by the probability that the metallic elements will do most of the work of current transfer in the spark flame, at a potential so low that the outer electrons of the nonmetals will not be disturbed.

The internal standards method of Gerlach and Schweitzer (*4*) has been successfully applied to the quantitative analysis of practically all of the minor constituents of steels except carbon (*10*).

The authors applied the same method to the determination of carbon in steel. The relative line intensities of carbon and iron were determined by the logarithmic wedge sector (*9*, *11*), rotated before the slit of a Hilger E 1 Littrow quartz

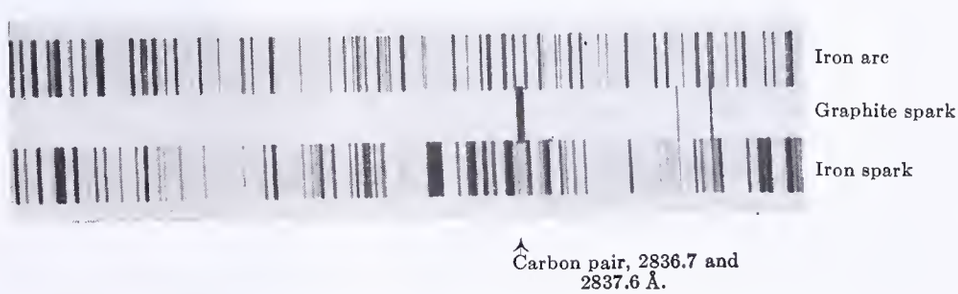

Figure 1

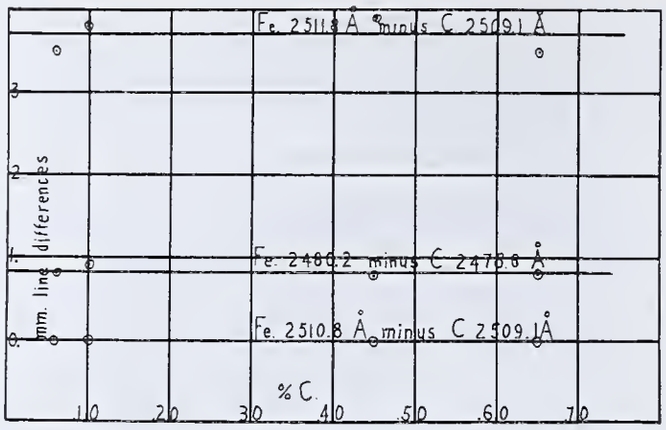

FIGURE 2. RELATION BETWEEN PERCENTAGE OF CARBON IN STEEL AND DIFFERENCE IN LENGTH OF SELECTED IRON AND CARBON WEDGE SPECTRUM LINE PAIRS

spectrograph. The instrument was set to take the region between 2250 and 2850 Å. According to Kayser and Konen (*6*), the following lines are given by carbon in the ultraviolet:

Å.[a]	Estimated Intensity Spark	Arc
2992.6	1	–
2837.6	3	1
2836.7	7	1
2747.3 } 2746.5 }	3 diffuse	–
2512.0	5	1
2509.1	4	1
2478.6	10	10
2296.8	8	1

[a] The carbon line 2641 Å. given by Kayser (*5*) and the carbon lines 2547.8, 2402.4, and 2401.77 Å. given by Fowler (*3*) were not found in a graphite spark spectrogram.

All these lines appear in a graphite spark, but only three were found in sparks from samples of steels: at 2296.8, 2478.6, and 2509 Å. The line at 2296.8 Å. coincides with a faint iron line, which is of constant intensity and so faint that it will not interfere with the use of this carbon line at 2296.8 Å. for quantitative analysis of carbon in steel. The carbon line at 2478.6 is interfered with by the Geisler tube oxygen line at 2478.5 Å. Oxygen will not interfere, provided the oxygen lines at 2445.5 and 2433.6 Å. are not visible. The carbon line at 2509.1 Å. has no listed interferences. Although unmarked iron lines are very close, the carbon II pair 2836.7 and 2837.6 Å. are shown by the comparison spectrum in Figure 1 to be absent from the iron spark. This is remarkable, since the carbon III line at 2296.8 Å. is easily seen.

A series of steel samples varying in carbon content from 0.05 to 1.02 per cent was subjected to various combinations of sparking and arcing conditions. These experiments (Table I) amply demonstrate that carbon in steel shows no concentrational variation by ordinary spectrographic methods (Figures 2 and 3). The spectrograph frequently brings out variations in concentrations less than 0.05 per cent, even when it does not in higher ones.

Accordingly a series of samples was obtained which had been analyzed by vacuum fusion methods, and found to contain from 0.005 to 0.01 per cent of carbon. In order to activate the carbon in these samples, they were subjected to still more intense sparks (second part of Table I). The 0.005 per cent carbon sample, which shows an increase in carbon line in-

TABLE I. SPECTROGRAPHIC DETERMINATION OF CARBON IN STEEL

Method	Conclusions
Carbon content 0.05 to 1.02 per cent	
Equal weights of wires of varying carbon content were completely burned in 200 seconds in a 3-ampere arc. Upper electrode negative and of magnesium. Lower electrode positive and a measured length of the sample. Upper electrode made large enough so that it did not melt or burn.	Intensity of carbon lines relative to iron lines varied solely with the gap length, becoming weaker with longer gaps. No concentrational variation.
Spark between two electrodes of the sample. Gap 1.5 cm.; 1-kw. 15,000-volt transformer; 10-microhenry inductance; 0.009- to 0.036-microfarad capacity. Resistance up to 50 ohm.	Intensity of carbon lines relative to iron lines decreased with increasing inductance and resistance. Increasing capacity increases intensity of carbon lines relative to iron lines. No concentrational variation.
Carbon content 0.005 to 0.01 per cent	
Tesla coil spark 1-kw. 15,000-volt transformer, 0.018-microfarad capacity, fed primary of Tesla coil. Sample attached to secondary with 0.009-microfarad shunt, 2.5-cm. gap.	Long exposures (15 to 30 minutes) required. Carbon at 2478.6 Å. and oxygen at 2445.5 and 2433.6 Å. stronger than iron lines. No concentrational variation between 0.005 and 0.1 per cent carbon.
Aperiodic spark 1-kw. 15,000-volt transformer, 0.009-microfarad condenser. Inductance in oscillating circuit equaled that of leads which were about 30 cm. long. 2-cm. gap.	Spectra similar to that from Tesla coil, but more intense. Carbon line at 2478.6 Å. shows concentrational variation relative to iron lines. The line at 2478.6 Å. is stronger in the sample having the lowest amount of carbon (0.005 per cent).
Aperiodic spark in argon Same electrical conditions as above. Spark atmosphere consisted of 99.8 per cent argon which had been scrubbed with BaO, NaOH, and phosphorus pentoxide.	Carbon lines stronger relative to iron lines than by any other method. Wandering of spark makes equivalent exposures impossible.

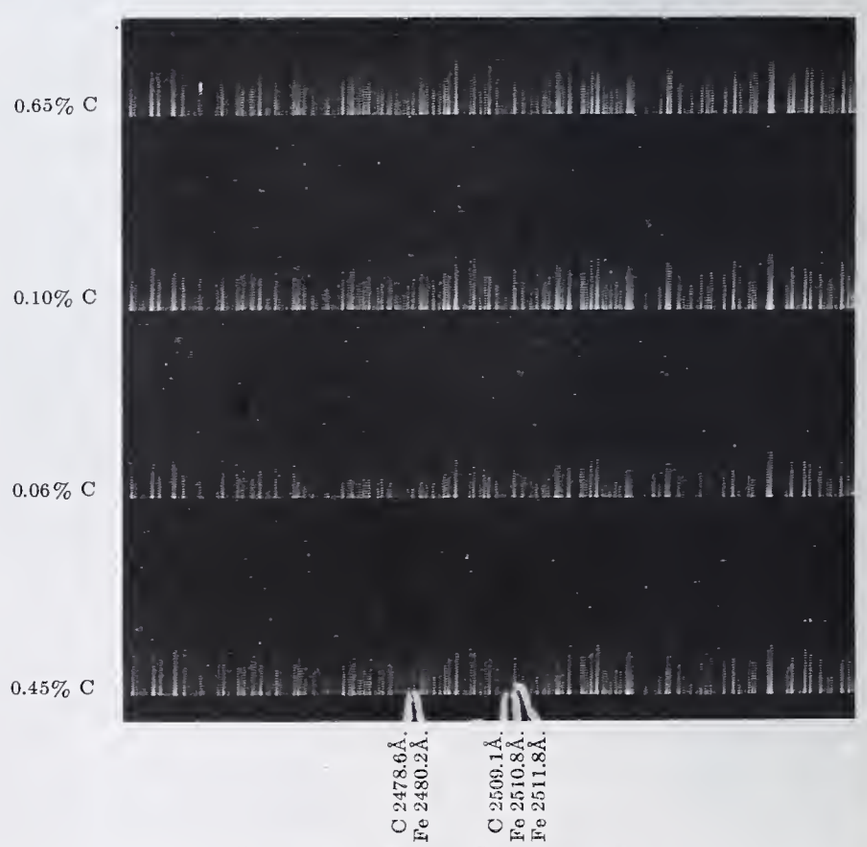

FIGURE 3. WEDGE SPECTROGRAM

Made with a Hilger E 1 spectrograph and rotating logarithmic sector disk. Spark between steel electrodes recorded on Eastman 33 plate and developed in D 19. Circuit consisted of 1-kw. 15,000-volt transformer, 10-microhenry inductance, 0.018-microfarad capacity, with a gap of 1.5 cm.

tensity, had been treated with iron oxide and is higher in oxygen. An oxygen line appears at 2478.5 Å., and increases the intensity of the carbon line from which it is not separated. The oxygen lines at 2445.5 and 2433.6 Å. also show an increase in intensity as compared with higher carbon samples. The aperiodic spark is therefore capable of detecting concentrational variations in oxygen content, but these variations must be much greater than those normally experienced in steels. A sample of iron containing less than 0.005 per cent of carbon and low oxygen was made available. This sample was of high purity, and had been treated with wet hydrogen at 1495° C. for 61 hours. It probably contained about 0.001 per cent of carbon. Using the aperiodic spark, this sample was compared with a sample of steel containing 0.1 per cent of carbon. The carbon lines in the two samples are of equal intensity.

Conclusions

Although the aperiodic spark detects gross changes in oxygen content, it apparently does not have potential enough to bring out either small or large variations in carbon content. The problem of the spectrographic analysis of nonmetallics in metals may be solvable by using excitation which will ionize a high percentage of the metal atoms. Means of more intense excitation than the aperiodic spark are available in the exploded wire (*1*), the vacuum spark (*2*), and electric furnace arc (*7*, *8*) methods.

Acknowledgments

This work was made possible by a grant given by the National Smelting Co., Cleveland, Ohio, and was carried out on this company's spectrographic equipment. The following companies donated analyzed steel samples: The Cleveland Twist Drill Co.; Newburgh Works, American Steel and Wire Co.; and the Illinois Steel Co. Low-carbon samples were obtained from the Naval Research Laboratory and the Carnegie Institute of Technology.

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Spectrographic Microdetermination of Zinc

Preliminary Note

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INTEREST of biologists in the physiological effects of small amounts of zinc on plants and animals has prompted a study of the applicability of spectrography to the quantitative determination of this element.

For the spectrographic detection of zinc, various workers have used three lines in the zinc spectrum—namely, those occurring at 4810.534, 3345.0, and 2138.5 Å. Early in this investigation, it was found that zinc was not detected in many of the samples which were examined when only the first two of these lines were used, because they are not sufficiently sensitive to give an observable density on the photographic plate with very small concentrations of zinc. The 2138.5 Å. zinc line, however, proved to be quite sensitive. Since calcium and strontium are common constituents of plant materials, a spectrograph with good dispersion is necessary to separate the 4810.534 Å. zinc line from the 4811.86 Å. strontium line, and the 3345.0 Å. zinc line from the 3344.49 Å. calcium line.

For the 2138.5 Å. zinc line to register on the photographic plate, it is necessary to sensitize it in some manner. A plate sensitized by spreading ordinary mineral oil over the emulsion is satisfactory, but the Eastman spectroscopic plate, Type III-O, with ultraviolet sensitization is more convenient.

Of the various methods of quantitative spectrum analysis, it was decided to follow that of Nitchie and Standen (*2*), substituting a nonrecording microphotometer for the recording instrument used by them.

Procedure

A base, free of zinc, and approximating a representative plant ash, was synthesized as follows (after first running a qualitative spectrographic analysis on the ingredients to insure absence of zinc): three grams of H_3PO_4, 3.5 grams of Na_2CO_3, 5 grams of $MgCl_2 \cdot 6H_2O$, 10 grams of $CaSO_4 \cdot 2H_2O$, and 32 grams of K_2CO_3 were dissolved in water where possible, then evaporated while stirring, to insure homogeneity. After drying, the mixture was thoroughly pulverized.

It was decided to use tellurium as the "internal standard" of the method, since a sensitive line of tellurium occurs at 2143.0 Å. Accordingly, 5 grams of $H_2TeO_4 \cdot 2H_2O$ were dissolved in 1 liter of water, filtered, and added to all samples and standards in the proportion of 1 ml. of solution to 1 gram of sample.

For a stock zinc solution, 0.8797 gram of $ZnSO_4 \cdot 7H_2O$ was dissolved in 1 liter of water. Five milliliters of this solution were added to 1 gram of the synthetic ash, plus 1 ml. of the tellurium solution, dried, then thoroughly pulverized and mixed to give a standard containing 0.1 per cent of zinc. Other mixtures, prepared by adding 5 ml. of the proper dilution of the stock zinc solution and 1 ml. of the tellurium solution to 1-gram portions of synthetic ash, gave standards containing 0.05, 0.01, and 0.005 per cent of zinc.

Each standard was spectrographed in quintuplicate under the following conditions:

About 20 mg. of the standard were placed in the lower (positive) electrode of Acheson graphite rod 0.63 cm. (0.25 inch) in diameter and 3.8 cm. (1.5 inches) long, bored to a depth of 0.32 cm. (0.125 inch) with 0.436-cm. (0.172-inch) drill, and burned to completion with an arc drawing 9 amperes and a direct current line voltage of 125. A quartz Leiss spectrograph which disperses the spectrum from 2100 to 8000 Å. on one 22.5-cm. (9-inch) plate was used. A rotating sector wheel with adjustable aperture was inserted between the arc and the slit of the spectrograph to reduce the exposure 75 per cent.

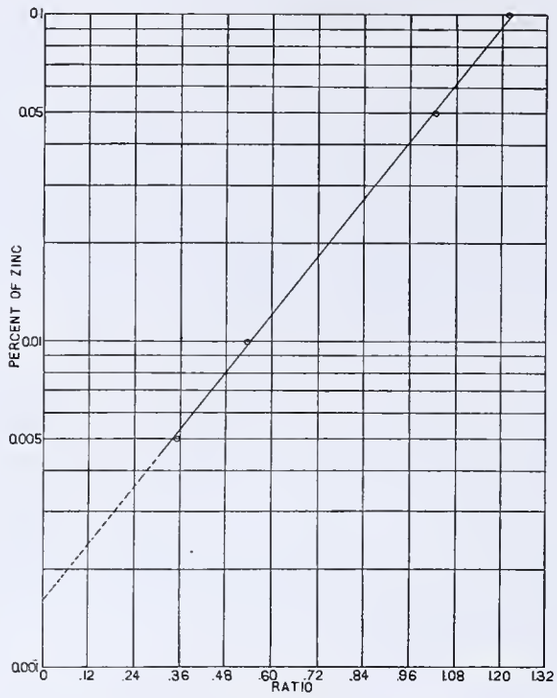

FIGURE 1. CALIBRATION CURVE

The spectrograms were photometered on a Bausch & Lomb density comparator. The ratios of the densities of the 2138.5 Å. zinc line and the 2143.0 Å. tellurium line for the various standards thus determined were averaged and plotted on semi-logarithmic coördinate paper with the result shown in Figure 1.

PREPARATION OF SAMPLES. In preparing the plant samples for analysis, they were first dried, and then ashed at less than 450° C. in platinum, at which temperature, according to Thompson (*3*), zinc is not volatilized. Tellurium solution was added to the ash, then it was dried, pulverized, mixed thoroughly, and spectrographed in quintuplicate under the same conditions as given for the standards.

TIME FOR ANALYSIS. Neglecting the time required for ashing the samples, adding tellurium solution, drying, and homogenizing, 2 hours are ample for making ten spectrograms—i. e., two samples in quintuplicate—developing, fixing, washing, and drying the plate, and an additional 1.5 hours are sufficient for photometering and conversion of the ratios to percentages.

Limits of Method

The upper limit of the method is not 0.1 per cent although at about 1 per cent the 2138.5 Å. zinc line begins reversing; hence for percentages greater than this, other lines would have to be used, probably that line occurring at 4810.534 Å. The lower limit is not necessarily 0.005 per cent, for assuming that the calibration relation holds below this concentration, extrapolation of the calibration curve would indicate sensitivity to about 0.002 per cent.

Interference

When appreciable iron is present in the sample, an iron line may occur at 2138.587 Å., which would be unresolved by most spectrographs from the 2138.5 Å. zinc line and thus lead to erroneous results. Preliminary tests indicate that from 0.5 to 1 per cent of iron is required to give an observable density of this iron line on the photographic plate. Burns and Walters (*1*) assign an intensity of three to this iron line, and to another iron line at 2132.011 Å. they assign an intensity of four. In this work, therefore, the plates were always examined for the presence of the iron line at 2132.011 Å., and since it has never appeared in any spectrogram of any sample, the possibility of an iron interference has been neglected. The study of this interference and the development of a method to permit allowance for the presence of iron is to be undertaken (probably using the ratio of intensities between the 2132.011 Å. iron line and the 2143.0 Å. tellurium line).

Accuracy

The large deviation from the mean of the last analysis in Table I is due either to lack of homogeneity of the sample or to the use of the extreme end of the calibration curve. The maximum deviation from the mean in most cases is less than one part in five. Handling all samples and standards in solution will probably reduce this deviation. Further study of the method is proposed to determine probable error. The influence (if any) of synthetic ashes of different composition is also to be studied.

TABLE I. QUINTUPLICATE ANALYSES OF SEVERAL SAMPLES

Ratio	Per Cent
0.471	0.0078
0.438	0.0070
0.415	0.0065
0.415	0.0065
0.451	0.0073
	Av. 0.0070 ± 0.0008
0.73	0.019
0.73	0.019
0.71	0.017
0.69	0.016
0.73	0.019
	Av. 0.018 ± 0.002
1.22	0.10
1.12	0.07
1.24	0.11
1.22	0.10
1.16	0.08
	Av. 0.09 ± 0.02

Summary

A quantitative spectrographic method for determining zinc in plant material when present in concentrations between 0.1 and 0.005 per cent, employing tellurium as an internal standard, has been studied. Iron interferes with the determination when present in concentrations of about 1 per cent, and a procedure for making allowance for this interference is suggested. The maximum deviation of the analyses from the mean in most cases is less than one part in five. Further study of the method is proposed to determine the probable error and influence of other factors on the procedure.

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RECEIVED June 7, 1935. Based upon a part of a Master of Science thesis submitted to the graduate council of the University of Florida, August, 1934, which was carried out under the direction of R. C. Williamson, University of Florida, and L. W. Gaddum, Florida Agricultural Experiment Station.

Correction

In the article on "Constituents of Pyrethrum Flowers" by Haller and Acree [IND. ENG. CHEM., Anal. Ed., 7, 343 (1935)] an error was made in citing the page in the first of the literature references given. The correct reference is Butt, C. A., J. IND. ENG. CHEM., 7, 130 (1915).

The Determination of Small Quantities of Selenium in Sulfur

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THE determination of very small quantities of selenium in various materials is becoming of increasing importance, as shown by recent articles on the determination of small amounts of selenium in pyrites, shales, soils, and agricultural products (*2*, *4*, *6*). In addition, the appearance of selenium in the 18-8 type steels in small percentages makes particularly desirable a reliable method for the determination of small amounts of this element. In this paper, the determination of small quantities of selenium in sulfur is reported over the range from 0.1 to 0.001 per cent. Smaller percentages could no doubt be determined by the use of a larger sample for analysis, but the range below 0.001 per cent was not investigated in the present work. A later communication will describe a convenient method for the determination of selenium in steels.

The present method was developed as a result of an investigation of Beattie, Benedict, and Blaisdell upon the intercomparison of the international and thermodynamic temperature scales from 0° to 444.6° C. (*1*). Sulfur vapor was used in this investigation, and it became necessary to know the amount of selenium present, if any, because of the effect upon the boiling point of sulfur. The method, as developed, requires a minimum amount of apparatus, and an analysis may be completed in about 3 to 5 hours; the detection and quantitative determination of 1 mg. of selenium in 100 grams of sulfur are possible. The method is applicable to all kinds of sulfur and sulfur-containing materials; arsenic and tellurium cause no interference; and large samples may be used, thereby allowing the determination of small percentages.

Most previous methods for the detection of selenium in sulfur have required the complete solution of the sulfur (*5*), which necessarily limits the size of the sample and therefore limits the determination of very small percentages of selenium. The only other method in the literature which is similar to the one given here and which employs a similar apparatus is a rather long and complicated procedure, with expensive equipment, and involves the use of concentrated solutions of potassium cyanide (*3*). Furthermore, this method has been found to be of questionable accuracy.

Experimental

In the proposed method, the sample is burned in a 45-mm. Pyrex glass tube 60 cm. (2 feet) long, and the selenium is caught in a suitable solid filtering medium and then converted into selenium dioxide, which is titrated by the iodometric method:

$$SeO_2 + 4HI \rightarrow Se + 2H_2O + 2I_2$$
$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

The sulfur used was the purest obtainable grade of sublimed sulfur. The selenium dioxide used was prepared from crude selenium dioxide by digestion with concentrated nitric acid, filtering, evaporating, crystallizing, and then subliming to give clear crystals of selenium dioxide. A standard solution of selenious acid (containing about 1 mg. of selenium per cc.) was prepared from this selenium dioxide, and standardized iodometrically against a carefully prepared solution of thiosulfate which had been checked against Bureau of Standards arsenic trioxide. In addition, the selenious acid solution was standardized by precipitation as selenium from a concentrated hydrochloric acid solution by means of sulfur dioxide. The two methods of standardization checked each other.

Tellurous acid solution was prepared by dissolving crystalline tellurium in concentrated sulfuric acid. This solution was diluted to a definite volume and standardized gravimetrically by precipitation of tellurium by means of sulfurous acid and hydrazine.

In order to obtain a definite quantity of selenium, the following procedure was used:

> A 10-cc. pipet of standard selenious acid solution was delivered into a 250-cc. beaker, 25 cc. of concentrated hydrochloric acid were added, followed by 25 cc. of hydrochloric acid saturated with sulfur dioxide, and the solution was allowed to stand at least 24 hours. At the end of this time, the red modification was completely precipitated and had settled out upon the bottom of the beaker. This precipitated selenium was then filtered upon asbestos or a layer of sulfur about 3.8 cm. (1.5 inches) thick. The red selenium was dissolved from the asbestos or sulfur pad by means of concentrated nitric acid, the solution concentrated to small volume, made alkaline with ammonium hydroxide to precipitate ferric hydroxide, and, after filtration, again acidified with nitric acid. Urea was added to destroy nitrous acid, the solution cooled, an excess of potassium iodide added, and the liberated iodine titrated with standard sodium thiosulfate. Using the same pipet in order to obtain the same quantity of selenious acid, hydrochloric acid and potassium iodide were added and the mixture was titrated with standard sodium thiosulfate solution. The two procedures required the same amount of sodium thiosulfate solution.

Of the reagents which might be used for the solution and oxidation of selenium to selenium dioxide, concentrated nitric acid was found to be the most satisfactory. Nitric acid solutions of selenium may be concentrated to a small volume with no loss of selenium, a fact which was checked by numerous experiments. None of the selenium is oxidized to selenic acid by either dilute or concentrated nitric acid. The one necessary precaution is the elimination of nitrous acid from the nitric acid just previous to the addition of potassium iodide and titration. Urea was found to be entirely satisfactory for this purpose. All experiments using urea gave excellent check results in varying concentrations of nitric acid.

The asbestos used for the plug in the end of the tube must be of the best quality and the usual laboratory grade requires further purification to eliminate iron. The procedure used to eliminate iron was to digest the asbestos fibers with concentrated hydrochloric acid for 4 to 5 hours, filter, wash, and dry at 110° C. This treatment reduced to a minimum the amount of iron that might later be extracted by the hot nitric acid.

A boat large enough to hold 100 grams of sulfur was required. To prepare this, Pyrex tubing of about 34-mm. bore and about 20 cm. (8 inches) long was closed at both ends and the upper part removed by melting away in an oxygen flame, thus producing a glass boat (Figure 1).

It was found after several experiments that the selenium dioxide gas badly attacked the rubber stopper used at the inlet end of the large tube. The best method for eliminating such attack was found to be that shown in the diagram. The oxygen gas passes in through the neck of the small, round-bottomed flask, thence through a hole in the neck of the flask into an oxygen chamber, and from there into the main com-

bustion chamber. This arrangement prevented any action upon the rubber stopper, even after months of usage.

Of the different filtering mediums tried, by far the most satisfactory proved to be asbestos fibers which had been treated by concentrated hydrochloric acid, as described above. Liquid absorbents were found to be inadequate.

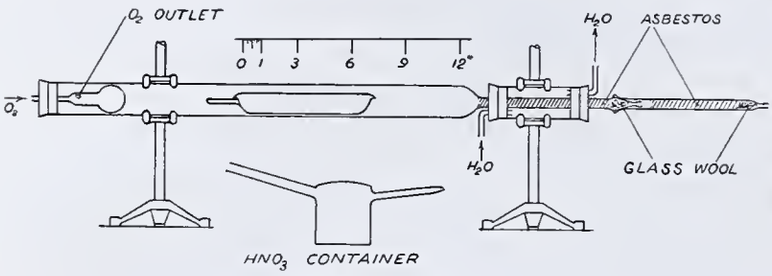

FIGURE 1

Constriction of the main tube at the exit end to a diameter of about 12 mm. permitted the use of an asbestos pad as long as 15 to 20 cm. (6 to 8 inches), without the use of an excessive amount of asbestos. At the end of the small tube the pad of glass wool prevented the possibility of blowing the asbestos out of the end. The constricted exit tube was cooled externally by means of a water jacket.

To the end of the small tube was attached an auxiliary tube filled with asbestos, a ground-glass joint between. This arrangement was found to be very useful whenever it became necessary to test the efficiency of any particular filtering medium. At the end of a run, the auxiliary tube could easily be examined for traces of selenium.

Another procedure, which proved useful in tracing the selenium at the end of the run, was developed. By passing sulfur dioxide gas through concentrated hydrochloric acid and then through the entire system, the selenium is almost completely precipitated in the red form, in which modification very minute quantities may be readily observed, a fact which proves to be very useful in testing the efficiency of different filtering mediums.

The color of the filtering mediums at the end of an ordinary run was a light green. After development of the red form, the efficiency of any particular filtering medium became evident from the extent of penetration of the red color through the mass of the filter.

A container suitable for handling hot, concentrated nitric acid was prepared from an ordinary 400-cc. tall-form beaker.

Procedure

The procedure adopted in the analysis of the seleniferous sulfur was as follows:

About 10 to 20 grams of the sulfur were placed upon a filter plate within a tall-form Gooch funnel, and tamped down to form a compact mass about 3.8 cm. (1.5 inches) thick. Upon this sulfur was filtered the known quantity of selenium, which had been precipitated from a concentrated hydrochloric acid solution by sulfur dioxide at least 24 hours previously. The filtered selenium was washed with hydrochloric acid, water, alcohol, and then ether. By pushing a stirring rod up through the stem of the funnel, the entire mass of sulfur, with selenium upon the surface, moved out through the straight sides of the funnel, cleaning the sides as it went. After drying at room temperature a few hours, the sulfur and selenium were mixed and transferred to the Pyrex boat. The small end chamber was prepared with the glass wool and asbestos filter. The apparatus was always tested with oxygen before starting a run, to be sure the asbestos was not too compact to prevent ready passage of gases. Furthermore, it was found desirable to have the main combustion chamber full of oxygen before placing the lighted sulfur in position.

The sulfur in the boat was lighted in a small spot, the boat immediately pushed into position, the chamber closed, and oxygen allowed to pass. The heat of combustion of the sulfur carries the reaction to completion. At the end of a run on a 100-gram sample of sulfur containing selenium, a small residue of a few milligrams would remain, and about 2 or 3 cc. of an oily, green solution of selenium in sulfur trioxide collected in the bottom of the chamber. The entire chamber was allowed to cool, with oxygen passing to sweep out excess sulfur dioxide. The boat was removed and rinsed off with hot, concentrated nitric acid into a beaker. The combustion tube was then placed in a vertical position upon a suitable filter flask, suction applied, and hot, concentrated nitric acid run down the inside of the chamber through the asbestos, followed by hot wash water. The asbestos filter pad remained in position and a clear, yellow solution of nitric acid containing selenious acid was obtained. To this solution were added the washings from the boat, and the entire solution was concentrated to a volume of about 10 cc. This was cooled and ammonium hydroxide added to precipitate ferric hydroxide, which was filtered off and washed. The solution was neutralized with nitric acid, and 10 cc. of concentrated nitric acid were added. The solution was diluted to 50 cc., about 3 grams of urea were added, and the solution was gently heated for 2 to 3 minutes, cooled, and diluted to 300 cc. Three grams of potassium iodide were added, and the solution was stirred for 1 to 2 minutes and titrated with the standard sodium thiosulfate.

Table I contains the results obtained by this procedure, when decreasing quantities of selenium were added to increasingly large quantities of pure sulfur.

TABLE I. ANALYSIS OF SELENIFEROUS SULFUR

Sulfur Taken	Selenium Added	$Na_2S_2O_3$ Required Theoretical	Actual
Grams	*Mg.*	*Cc.*	*Cc.*
10	11.4	40.3	40.50
10	11.4	40.3	40.40
25	11.4	40.3	40.20
25	11.4	40.3	40.50
50	11.4	42.90	43.00
50	11.4	42.90	43.10
100	11.4	42.90	43.10
100	11.4	42.90	43.10
100	5.6	22.30	22.40
100	5.6	22.30	22.40
100	1.14	4.40	4.50
100	1.14	4.40	4.50

In addition, the following experiments were carried out on sulfur specimens from different sources, using the same procedure as previously described:

One hundred grams of commercial grade Texas sulfur (flowers of sulfur) were burned and no selenium was found present.

One hundred grams of crude Louisiana sulfur containing an appreciable amount of oil and hydrocarbons gave no selenium.

A 30-gram sample of crystal sulfur from Garginti, Sicily, gave no selenium.

Five-gram samples of seleno-sulfur of volcanic origin (Sicilian deposit) gave check results at 10.00 and 10.10 cc. of sodium thiosulfate, from which the selenium content was calculated to be 0.054 per cent. This sample contained a large percentage of arsenic, which caused no trouble.

EFFECT OF ARSENIC. The effect of arsenic upon the determination of selenium was tried by adding a definite amount of Bureau of Standards arsenic trioxide to a mixture of selenium and sulfur. The results obtained are shown in Table II where the amount of arsenic trioxide added was of the same magnitude as the selenium present, the same procedure being followed as before. These results led to the conclusion that moderate amounts of arsenic caused no trouble in the titration for selenium.

TABLE II. SULFUR CONTAINING SELENIUM AND ARSENIC TRIOXIDE

Sulfur	Selenium	As_2O_3	$Na_2S_2O_3$ Required Theoretical	Actual
Grams	*Mg.*	*Mg.*	*Cc.*	*Cc.*
25	11.4	10	42.90	43.10
25	11.4	10	42.90	43.20

EFFECT OF TELLURIUM. The selenium was precipitated in the usual manner and the tellurium was precipitated from a definite amount of prepared tellurous acid solution by means of sulfurous acid and hydrazine.

The tellurium and selenium were filtered on a mat of sulfur, and the mixture was burned in the usual manner. When tellurium was present, the inside of the combustion tube was coated over

with an opaque deposit of tellurium dioxide. The entire tube was washed out with hot nitric acid, as described above. The combined filtrates were evaporated to a volume of 10 cc. and carefully neutralized with ammonium hydroxide to the appearance of a precipitate of tellurium dioxide. Six cubic centimeters of 6 *N* nitric acid and 3 grams of urea were added and diluted to a volume of 300 cc. Three grams of potassium iodide were added, allowed to stand 7 minutes, 75 to 100 cc. of water were added, and the solution was titrated with sodium thiosulfate in the usual manner.

The end point was very satisfactory, but not as sharp as with selenium alone. The concentrations as given were found to be the proper ones to allow a titration of the selenium alone, without interference from the tellurium present. Variation of the acid concentration, iodide concentration, or time from those specified gave varying results, due to interference by the tellurium.

Table III. Effect of Tellurium

Sulfur	Selenium	Tellurium	$Na_2S_2O_3$ Required Theoretical	Actual
Grams	*Mg.*	*Mg.*	*Cc.*	*Cc.*
25	11.4	12.4	42.90	43.00
25	11.4	12.4	42.90	43.10

Summary

A procedure is described whereby amounts of selenium in sulfur ranging from 0.1 to 0.001 per cent may be accurately determined. Quantities of arsenic and tellurium present in magnitude equivalent to that of the selenium were found to cause no interference. The apparatus required is simple in construction, the number and quantity of reagents used are a minimum, and the total time required is a matter of a few hours. The reproducibility of results is quite satisfactory, if the usual precautions of analysis are observed.

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Boron Content of Sea Water of the North Atlantic Coast

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SOME time ago Moberg and Harding published a brief account of determinations of the boron content of sea water (*1*). Their samples were for the most part drawn from the Pacific. Because of the part which boric acid presumably plays in the buffer mechanism of sea water it is important to know how uniformly it is distributed, and it was therefore thought desirable to make similar determinations on water of the North Atlantic coast. Accordingly, the same method used by Moberg and Harding (a modification of the differential electrometric titration described by Wilcox, *2*) was applied to some 75 samples from different depths at eight stations along the Atlantic coast, within cruising range of Woods Hole.

The stations may be divided into two groups: Nos. 1731, 1732, 1734, and 1739 to the south of Cape Cod in the direction of Bermuda, at which the water is of generally southern origin; and Nos. 1747, 1767, 1775, and 1781 in the Gulf of Maine, at which the water is of generally northern origin. The average boron concentration in the 39 samples from the southern stations is almost identical with that in the 36 samples from the northern stations, being 4.73 mg. per kg. in the former and 4.75 mg. per kg. in the latter. This compares with an average of 4.50 mg. per kg. found by Moberg and Harding.

More important, however, is the ratio of boron to chloride (or total halide). The average ratio, B/Cl, at the southern stations was 0.000240, almost identical with 0.000239 found by Moberg and Harding in their fifty samples. At the northern stations a B/Cl ratio of 0.000255 was found, indicating a slightly higher percentage of boron in the dissolved solids of the water of this region.

There seems to be no significant regularity in the vertical distribution of boron.

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Table I. Boron in Sea Water

Depth	Boron	Ratio
M.	*Mg./kg.*	B/Cl
Station 1731 38° 06′ N., 68° 54′ W.		
0	4.69	0.000236
30	4.64	0.000234
50	4.85	0.000243
60	4.85	0.000243
80	4.82	0.000241
100	4.93	0.000244
150	4.87	0.000240
200	4.92	0.000244
355	4.92	0.000250
530	4.87	0.000251
700	4.88	0.000252
860	4.79	0.000247
1020	4.82	0.000249
1175	4.77	0.000246
1320	4.71	0.000243
1685	4.74	0.000245
Station 1732 37° 21′ N., 68° 31′ W.		
0	4.45	0.000224
50	4.55	0.000229
100	4.67	0.000233
1050	4.62	0.000238
1725	4.67	0.000241
2710	4.52	0.000234
3830	4.58	0.000238
Station 1734 36° 27′ N., 68° 38′ W.		
0	5.07	0.000254
50	5.01	0.000243
87	4.97	0.000245
175	4.76	0.000236
365	4.72	0.000234
550	4.61	0.000229
730	4.56	0.000230
915	4.68	0.000239
1550	4.48	0.000232
2000	4.66	0.000241
3500	4.47	0.000231
Station 1739 40° 18′ N., 70° 22′ W.		
10	4.58	0.000250
30	4.31	0.000237
40	4.56	0.000250
60	4.31	0.000237
75	4.54	0.000247
Av.	4.73	0.000240
Station 1747 42° 41′ N., 69° 29′ W.		
0	4.42	0.000252
10	4.46	0.000255
28	4.42	0.000249
47	4.48	0.000250
73	4.54	0.000252
110	4.60	0.000253
150	4.74	0.000256
185	4.78	0.000255
240	4.73	0.000251
Station 1767 44° 11′ N., 66° 51′ W.		
0	4.48	0.000249
10	4.52	0.000251
30	4.59	0.000254
50	4.67	0.000256
80	4.83	0.000264
125	4.84	0.000261
175	4.83	0.000259
Station 1775 43° 13′ N., 65° 38′ W.		
0	4.40	0.000257
10	4.46	0.000259
20	4.48	0.000257
30	4.61	0.000265
40	4.57	0.000260
50	4.69	0.000264
Station 1781 41° 52′ N., 65° 10′ W.		
0	5.00	0.000261
20	4.90	0.000252
40	4.89	0.000251
59	4.94	0.000252
100	5.00	0.000254
150	4.97	0.000251
200	5.02	0.000254
300	4.92	0.000252
400	4.92	0.000254
600	5.02	0.000260
1000	4.95	0.000256
1395	4.86	0.000251
1800	4.94	0.000256
2000	5.06	0.000262
Av.	4.75	0.000255

Detection of Adulteration in Maple Sirup

A Simplified Rapid Method Based on Electrical Conductivity

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IN HANDLING large commercial volumes of maple sirup, the detection of adulteration is difficult because of (1) the smallness of the unit volume to be sampled, never over 55 gallons and often as little as 5 gallons; (2) the length of time required for chemical determinations, such as ash values, malic acid value, and even lead numbers; and (3) the wide variations in the values found in pure maple sirups.

Of the various official methods by means of which the purity of maple products can be determined, only one is suited for rapid manipulation with little loss in accuracy. This is the measurement of electrical conductivity, introduced by Snell (*3*), who pointed out that maple sirup showed a maximum conductivity when diluted with two volumes of water. The official method (*1*) adopted specified that the sample used be 22 grams of dry matter in a volume of 100 cc. This weight was subsequently changed to 25 grams (*2*) in order that a portion of the same sample might be used for Canadian lead number determination. The limitations of electrical conductivity methods have been described by Snell (*3*).

Method and Apparatus

The method proposed here was designed primarily to detect adulteration with white sugar, and is similar to the original method of Snell (*3*) except that the apparatus consists of a Leeds & Northrup sugar ash bridge and conductivity cell. No constant-temperature bath is necessary with this apparatus, since a knob on the bridge provides for variations in cell temperatures between 10° and 35° and variations in cell constant from 0.14 to 0.16, and all results are automatically corrected to 20°. The sirup is diluted with three volumes of water instead of two because the sample bottles in which the sirups are graded for color and in which they are received by the laboratory contain approximately 25 cc. This volume, diluted to 100 cc. with water, is sufficient both for rinsing the electrodes of the cell and filling the cylinder in which the electrodes are inserted. Density variations in the sirups and the presence of suspended "niter" may be neglected.

The rapidity of the method is its most important feature, and makes it particularly useful when a large number of samples must be examined. The method outlined above is far more rapid than any previously described. Two operators, one preparing the samples and the other taking measurements, can easily examine 400 or more samples per day.

PROCEDURE. Place 75 cc. of water in a 100-cc. graduated cylinder, add 25 cc. of sirup, and mix thoroughly. Rinse off the electrodes with approximately 40 cc. of this solution, pour the remainder into the testing cylinder, and insert the electrodes and thermometer. Adjust the temperature-compensating knob on the bridge to correspond with the cell reading, place the resistance plug in the proper setting (usually the 1000-ohm block), press the alternating current button, and turn the main slide-wire knob until the galvanometer balances. Take the dial reading. The product of this value and the plug setting is specific conductance multiplied by 10^6 and reduced to 20°. Since the conductivity value is defined as the specific conductance multiplied by 10^5, the product is 10 times the desired figure. The official method (*1*) also specifies 25° as the temperature for taking measurements, but 20° is fully as satisfactory provided the difference in conductance caused by the 5° change is taken into consideration.

ACCURACY OF METHOD. That the accuracy of conductivity measurements is not impaired by not weighing the sirup sample or reducing all sirups to a standard density was pointed out by Snell (*3*) and is further demonstrated by the following figures, showing the difference in conductivity values of sirup samples containing 25 grams of dry matter and 25 cc. of sirup (about 22 grams of dry matter) in a total volume of 100 cc. at 20°.

TABLE I. CONDUCTIVITY VALUES

25 Grams of Dry Matter	25 Cc. of Sirup
138	136
129	127
110	109
140	136
124	121
126	124

There is, of course, a considerable difference between the conductivity value measured at 20° and at 25°, but all values obtained at the same temperature are comparable among themselves and with the minimum standard chosen for that temperature. Measurements made at 25° average about 13 per cent higher than those made at 20°.

Range of Values

Because of the varying nature of maple products, it is impossible absolutely to define the two limits between which the conductivity values of pure maple sirups will fall. Snell (*3*) originally adopted 110 as the lower limit and 200 as the upper, but later (*4*) found values as low as 96 and as high as 230. His measurements were made at 25° on sirups known to be genuine. For the present study of over 7200 samples obtained from nearly all important producing sections in the United States and Canada the author has adopted for the method outlined above a minimum value of 100. However, a number of sirups with conductivity values lower than 100 were found which, by other methods, were considered either pure or doubtful. It should be emphasized here that sirups showing conductivity values near the minimum should always be examined by other standard tests before drawing conclusions regarding their genuineness. Since there was no guarantee of genuineness with any of the samples tested, the collected data cannot be used to help define the conductivity limits of pure maple sirup. Values found ranged from 40 in highly adulterated sirups up to 200, which corresponds closely to the maximum of 230 at 25° found by Snell.

TABLE II. CONDUCTIVITY VALUES

Source	No. of Samples Averaged	Grade	Conductivity Value
Canada (Quebec)	400	Mixed	144
United States:			
Maryland, Pennsylvania, New York, Vermont, and New Hampshire	500	Mixed	130
Maryland, Pennsylvania, and western New York	250	Mixed	135
Vermont, New Hampshire, and eastern New York	250	Mixed	124
Southeastern Vermont	100	Fancy and No. 1	130
Vermont and New York	250	Fancy	118
Vermont and New York	250	No. 3	137
New York	150	Mixed "Buddy"	142

Table II gives average values for various grades of sirups from various localities. These figures were selected at random from the large number at hand. All measurements were made at 20°.

Conclusions

The average conductivity value of Canadian sirups is higher than that of American sirups.

Sirups originating in Maryland, Pennsylvania, and southwestern New York show higher average conductivities than those from eastern New York, Vermont, and New Hampshire, with the exception of those from southeastern Vermont.

The average value for light-colored sirups is lower than that for the darker sirups.

"Buddy" sirups, regardless of color, usually show higher conductivity values than normal sirups.

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Bismuthate Method for Manganese. II

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IN THE reaction between arsenite and permanganate in acid solution used in the bismuthate method for manganese, the manganese is not reduced to the bivalent state (*4, 5, 7, 9, 10, 14, 17*).

Lang (*13*) has shown that a dilute solution of potassium iodate catalyzes this reaction and causes it to proceed according to the equation $2Mn^{+++++++} + 5As^{+++} \rightarrow 2Mn^{++} + 5As^{+++++}$ if the permanganate is added to the arsenite in either sulfuric or hydrochloric acid solution. Cantoni (*1*) proposed the addition of one drop of 0.1 per cent potassium iodide solution as catalyst. Lang (*12*) studied this procedure. Swift and Gregory (*16*) make use of iodine monochloride in hydrochloric acid solution. Gleu (*6*) proposed the use of 0.01 *M* osmium tetroxide in sulfuric acid solution.

Because the bismuthate method is usually carried out in nitric acid solution, it was thought advisable to test these catalysts in its presence. For this work an electrotitration outfit similar to that described by Kassner, Hunze, and Chatfield (*11*) was set up with the following modification: The 201-A tube was replaced by a Cunningham C-33 tube, the two platinum electrodes were replaced by one platinum and one tungsten, and a milliammeter with a large scale was employed. This set-up was found to be extremely sensitive and it was very easy to determine the end point within one drop of the very dilute solutions used.

Preparation of Solutions

Standard Arsenite. Bureau of Standards arsenious oxide No. 83 (1.8019 grams) was dissolved in water by the addition of a little sodium carbonate and diluted to 2 liters. The per cent purity of this sample, obtained by titration, is given on the certificate as 99.97. This figure is based on calculations made with the 1925 atomic weights. Recalculating on the basis of the 1935 weights gives a value of 99.93 per cent which was used.

Standard Permanganate. A well-aged strong solution was diluted with distilled water in the ratio of 1 to 10 and then restandardized frequently with Bureau of Standards sodium oxalate No. 40a. The results obtained corroborate the work of Halverson and Bergeim (*8*). After standing only 15 minutes the dilute solution was 0.5 per cent weaker than the value calculated from the strong solution. Four days later it was 1 per cent weaker than the calculated value.

Nitric Acid. Ordinary c. p. nitric acid was freed from oxides of nitrogen by blowing air through it as proposed by Cunningham and Coltman (*3*).

Experimental Results

All titrations were carried out electrometrically, the drop which caused the largest deflection being taken as the end point. Twenty-five cubic centimeters of arsenite solution were pipetted out and the volume was made up to about 200 cc. The other conditions were as noted in Table I. On the basis of this work a modification of the procedure for the bismuthate method in iron and steel is proposed.

After filtering out the excess bismuthate on a Jena glass filter No. 4, add the filtrate to a measured excess of standard arsenite solution containing 3 drops of 0.01 *M* osmium tetroxide and titrate with standard permanganate to the electrometric end point. (Cheishvili (*2*) has shown that washed and ignited asbestos reduces a small amount of permanganate when used as a filtering medium.) Bureau of Standards steel No. 65a was run by this method with the following results: found, 0.746 and 0.743 per cent of manganese. The certificate gives 0.746 per cent of manganese.

Bureau of Standards Norrie iron ore No. 28 was run by the bismuthate method as modified by Park (*15*), using arsenite with the addition of osmium tetroxide instead of ferrous ammonium sulfate. The results obtained were 0.442 and 0.438 per cent of manganese. The average value for manganese as given by the certificate for all methods is 0.465 per cent. Blum found 0.44 per cent by the bismuthate method.

Table I. Experimental Results

Catalyst	Acid	Ratio Calculated	Ratio Determined	Difference, P. p. 1000
KIO_3[a]	10 cc. H_2SO_4	1.004[b]	Uncertain[c]	...
KIO_3 + NaCl[d]	10 cc. H_2SO_4	1.004	1.004	None
NaCl[e]	10 cc. H_2SO_4	1.004	1.006	+2
NaCl + I_2[f]	10 cc. H_2SO_4	1.004	Uncertain[c]	...
I_2[g]	10 cc. H_2SO_4	1.004	1.022	+18
OsO_4[h]	10 cc. H_2SO_4	1.004	1.0048	+0.8
OsO_4 + NaCl[i]	10 cc. H_2SO_4	1.004	1.0048	+0.8
KIO_3[a]	15 cc. HNO_3	1.008	Uncertain[c]	...
I_2[g]	15 cc. HNO_3	1.008	Uncertain[c]	...
OsO_4[h]	15 cc. HNO_3	1.008	1.010	+2

[a] One drop of 0.0025*M* solution.
[b] From weights of As_2O_3 and $Na_2C_2O_4$ standardization of $KMnO_4$.
[c] No determinable end point.
[d] One drop of 0.0025*M* solution plus 1 gram of NaCl.
[e] 1 gram of NaCl.
[f] 1 gram of NaCl plus small crystal of I_2.
[g] Small crystal of I_2.
[h] Three drops of 0.01*M* solution.
[i] Three drops of 0.01*M* solution plus 1 gram of NaCl.

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Determination of Chlorine in Organic Compounds

I. A Rapid Lamp Method

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IN THE course of a study of the decomposition of organic sulfur compounds by means of aluminum chloride, it was noted that the sulfur values rose above 100 per cent as determined by the well-known lamp method for the determination of sulfur (*1*). Suspicion fell on chlorine as the cause, and led to the confirmation that many organic chlorine compounds form hydrochloric acid practically quantitatively on combustion under the conditions of the method. Under more restricted conditions other types form hydrobromic, hydriodic, and nitric acids along with the free halogen. This paper presents data with particular attention to carbon tetrachloride and phenyl chloride, which were used for studying the principal factors.

Experimental

GENERAL PROCEDURE. The organic compound is dissolved in a combustible solvent in various concentrations, preferably to produce 0.2 to 0.3 per cent chlorine, and is burned in the standard sulfur lamp following the precautions officially recommended by the A. S. T. M. (*1*). The titrations are made with precisely the reagents specified by the method with the same indicator. About 1 gram of solution is burned. The standard calculation may be used and a correction applied—namely, that 1 per cent of sulfur is equivalent to 2.216 per cent of chlorine.

TABLE I. DETERMINATION OF CHLORINE

Solvent	Compound	Halogen Calculated	Halogen Found	No. of Observations
		%	%	
Extraction naphtha	Phenyl chloride	0.069	0.069 ± 0.002	6
		0.121	0.121 ± 0.002	7
		0.124	0.123 ± 0.004	10
		0.276	0.273 ± 0.004	8
		0.524	0.504 ± 0.005	8
Methanol	Phenyl chloride	0.200	0.196 ± 0.003	4
Extraction naphtha	Carbon tetrachloride	0.072	0.073 ± 0.002	8
		0.130	0.132 ± 0.002	10
		0.260	0.263 ± 0.003	8
		0.390	0.394 ± 0.004	7
		0.520	0.522 ± 0.005	6
Methanol	Carbon tetrachloride	0.200	0.203 ± 0.003	4
Methanol	Ethylene Chlorohydrin	0.353	0.345 ± 0.005	2
Extraction naphtha	*o*-Chlorophenol	0.177	0.176	2
	Hexachlorobenzene	0.068	0.069 ± 0.007	4, crusts
	Epichlorohydrin	0.168	0.178 ± 0.005	2
	Ethylchloroacetate	0.256	0.270 ± 0.010	4, smoke
	Chloroacetone	0.162	0.168 ± 0.010	4, smoke
	Ethylene dibromide	0.427	0.277 ± 0.004	2
	Ethyl iodine	0.273	0.302 ± 0.005	2
	Hydrazobenzene	0.015	0.009 ± 0.002	2
Methanol	Isoamyl nitrite	0.195	0.163 ± 0.003	2

Discussion

The choice of a hydrocarbon solvent should fall on a petroleum fraction relatively free of sulfur and somewhat lighter than gasoline. The material used in this investigation contained 0.018 per cent sulfur. The analysis was checked at 5 points in the investigation, so that the value is an average of 10 determinations to within 0.001 per cent. This served as a blank correction. In the case of methanol the blank correction was zero.

The lamp method operates best in solutions less concentrated than 0.5 per cent, preferably at the 0.1 to 0.3 per cent level, where the determinations are good to 2 to 3 per cent. Therefore, since burning about 1 gram suffices, a determination can be carried out with only a few milligrams of a substance.

The results for phenyl chloride tend to be slightly low, the effect rising to about 4 per cent at the highest concentration used. The results for carbon tetrachloride are slightly high in every case, but to the extent of only 1 per cent, and this may be attributed to difference in volatility. The other chlorine compounds have not been studied in detail, but the author hopes that further experience will lead to better adjustments. For example, the low solubility of hexachlorobenzene in naphtha led to crust formation and some erratic results, a good average being, in his opinion, more or less of an accident. Furthermore, smoky experiments should probably be discarded, although they were included in this report.

The fact that check values have been obtained for the combustion of compounds containing bromine, iodine, and nitrogen, although they are quite different from the amounts actually introduced, raises some hope for further study of the proper conditions of combustion to insure complete conversion to acids. The addition of hydrogen peroxide to the carbonate absorber is a possible method in the author's opinion, judging from the known reducing action of peroxides on free halogens.

The author's 112 determinations are in general accord with 43 determinations reported by Wirth and Stross (*6*) on amyl chloride, amylene dichloride, benzyl chloride, butyl chloride, carbon tetrachloride, dichlorobenzene, ethylene dichloride, isopropyl chloride, isobutyl chloride, and propyl chloride, in gasoline to chlorine concentrations of 0.017 to 0.390 per cent, by the use of Mohr's method of titration with silver nitrate following the combustion. Bowman (*2*) also uses a combustion method, determining chlorine nephelometrically and finding it necessary to ash the wick. Miloslavsky and Vepritzkaya (*4*) have carried on some combustions of alcoholic solutions, catching the hydrochloric acid in silver nitrate and titrating the excess silver nitrate with potassium thiocyanate. Using a Kennedy lamp (*3*), similar to the standard, Smith (*5*) records a few satisfactory determinations of chlorine in pinene hydrochloride and in mono- and dichlorobenzene dissolved in turpentine, by a silver chloride determination of the absorbed products of combustion. The author's work indicates that a simple titration is sufficient when dealing only with chlorine. Specific applications must await empirical trial, since no general rule can be given on the basis of several compounds.

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Notes on the J. Lawrence Smith Fusion

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There have been pointed out several sources of possible disagreement between different analysts over the alkali content of the same material when using the standard J. Lawrence Smith fusion. Since different substances are not thereby decomposable to the same extent, it has been suggested that the samples first be ground to some standard size, that the fusions be made at a higher temperature than is now customary, that the calcium carbonate and ammonium chloride flux be mixed together by ball-milling, and that correction of the mixed chlorides for accompanying magnesium be appropriately emphasized. The suggested improvements have been applied in the analysis of so-called beta-alumina.

As MANY prominent analysts continually fail to agree on the alkali content of rocks, minerals, refractory substances, and the like, and report different results on one and the same material after preliminary treatment by the J. Lawrence Smith method of fusion, it has been thought worth while to describe some of the experiences met in the Norton Company Research Laboratories with the J. Lawrence Smith treatment of difficultly attackable materials, in the hope that the results may lead to some improvement of the method as now standardized.

All the better texts on analytical chemistry that have come to the authors' attention emphasize the danger of losing gases, oxidizing the sample, and picking up moisture by grinding the sample excessively, but none mentions the fairly obvious fact that the less subject to attack a material is the more finely it must be ground to insure decomposition. Washington (*18*) and Hillebrand and Lundell (*8*) are among the few who adhere to Smith's (*17*) original directions in stating that the sample for a Smith fusion should be ground to an impalpable powder, although Smith himself states that such is not always necessary. The degree of fineness of a material expressed by a term like "impalpable powder" can be very loosely interpreted, depending on the individual and on the amount of labor involved in grinding the sample; a sample through 100-mesh on 120-mesh may be quite impalpable to most people, but will not always be completely decomposed by a single fusion. A glass is more readily decomposable than a clay or a feldspar, but spectrographic examination of residues shows that lepidolites through 100-mesh are not completely decomposed by one fusion. Beryl and tourmaline are more difficult to attack, and such substances as fused alumina are far more difficult still.

Hillebrand and Lundell (*9*) claim that a second fusion is seldom necessary, but state in a footnote that appreciable amounts of alkalies can be recovered from a second treatment of even so amenable a substance as a diorite. This lends support to the contention of Dittrich (*4*), Mellor (*13*), and Connor (*3*) that several milligrams of alkalies are not recovered after one treatment; whether or not all of the alkalies are recovered in a single treatment depends on the nature, particle size, and fusibility of the sample.

A second point upon which many chemists disagree is the temperature of fusion. Most of them state that if heated too hot the subsequent leaching is accomplished with difficulty; Washington (*18*) even claims that some alkali chloride may be lost by volatilization. The latter assertion is possibly true in the case of rubidium and cesium, but the average analyst is seldom concerned with more than sodium and potassium.

A third point is the manner in which the sample is mixed with the ammonium chloride–calcium carbonate fusion mixture. The standard procedure is to add the ammonium chloride to the sample, and then to incorporate the calcium carbonate, a process that cannot always insure the uniform formation of an ammonium chloride–calcium carbonate fusion mixture.

Analysis of Highly Aluminous Materials

The authors' experience with the J. Lawrence Smith fusion has been confined mainly to highly aluminous minerals of low silica content, both raw and calcined, and to electric furnace products consisting principally of fused alumina; all these materials are inherently much more difficult to decompose with ammonium chloride–calcium carbonate than the highly siliceous materials, such as rocks, usually examined for alkalies. In analyzing them for sodium and potassium it has been found (1) that comparable disintegrations by the J. L. Smith method can be obtained only when the samples have been ground to a comparable, controlled size; (2) that highly aluminous samples low in silica must be ground so that all the sample passes 200-mesh, and that an "impalpable feel" is not a sufficient criterion to insure complete decomposition; (3) that the highest temperature of a Méker-type burner is preferable for the fusion, and occasions neither loss of alkali nor difficulty in leaching the cake; and (4) that complete decomposition of the sample is not effected unless the ammonium chloride and calcium carbonate have previously been intimately mixed before compounding with the sample.

Complete disintegration of a difficultly decomposable substance is almost always effected when the sample has been ground to pass 200 mesh; it has been found, however, when a sample of fused alumina through 100 mesh is treated by the J. Lawrence Smith method, that from 20 to 60 per cent of the sample remains undecomposed after the first treatment, and that several subsequent treatments are necessary to decompose the sample completely. Microscopic and spectroscopic examination of the residues of feldspars and lepidolites, which are comparatively amenable to decomposition, has shown that under approximately the same conditions of fusion there is from 1 to 5 per cent of the sample undecomposed with one fusion after passing 100 mesh; at 150 mesh there appeared to have been complete decomposition; and samples through 200 mesh, even beryl and fused alumina, were completely decomposed after the first treatment. The retention of lithium by the sinter after complete decomposition of the sample has no immediate bearing on the question; it is being investigated and will be reported upon later. Smith (*17*) himself says that complete decomposition is seldom effected with one fusion of an impalpable powder; Mellor (*13*) adduces numerical data on the incompleteness of decomposition of such substances as basalts, syenites, etc.

Grinding a substance to impalpability can afford no assurance that the entire sample has been reduced to the fineness of the few portions that are felt. A method of analysis that is adopted as standard cannot be expected to yield satisfactory results when variables are introduced, such as inherent resistance of sample to fusion, particle size of sample, and temperature of fusion. Accordingly, if the J. Lawrence Smith fusion be expected to afford concordant results on the same materials in the hands of different analysts, some recommendation should be made to subject the sample at least to a uniform treatment that will insure complete decomposition.

In spite of the assertion by Washington (*18*) that some alkali chloride may be volatilized by heating the fusion too strongly with a Bunsen burner, there appears in the authors' hands to be no loss of alkali whatever from Bureau of Standards samples of feldspars, glasses, or clays, contained in standard J. L. Smith crucibles set up in the standard way, and heated with the conventional proportion of flux for twice the prescribed period with the hottest flame obtainable from a Méker type burner. The ammonia is first gently fumed off, and the lower portion of the crucible is brought, over a period of 20 to 30 minutes, to between 1000° and 1100° C., and is kept at that temperature for another 90 minutes. These temperatures were measured on the outsides of the crucibles by means of an optical pyrometer. It is true that sodium and potassium chlorides have an appreciable vapor pressure (*15*) at their melting points when alone, but such does not seem to be the case during a J. L. Smith fusion. If chlorides are volatilized in the hot zone, they are no doubt condensed in the upper part of the crucible, for the crucibles are tightly covered, the upper part of the crucible is considerably cooler than the lower portion, and the heating at the high temperature is not done until the evolution of gases has ceased.

The authors have found that decomposition of the less siliceous materials is invariably incomplete unless such temperatures are attained, and that two or even three Bunsen burners do not raise the entire lower portion of the crucible to the temperature required.

Following the ignition, there is very seldom any trouble in disintegrating the sinter, provided the recommendation of Mellor (*14*) is followed of adding not more than 2 ml. of hot water to the cake, and allowing it to stand for 10 to 15 minutes before adding more water. The slaking of the lime exerts a powerful disintegrating action on the cake if there is no excess of water to absorb the heat evolved. If, however, the cake is allowed to stand too long before beginning to extract it, it shows a tendency to go colloidal. Most difficulties in leaching the cake can be traced to improper mixing of the flux with the sample and to insufficient or improper heating of the fusion mixture, both of which cause incomplete decomposition.

Decomposition will still not be complete in the case of a very resistant material, even on a properly sized and thoroughly ignited sample, unless the fusion mixture has been specially prepared.

Willard (*20*) suggested that the calcium carbonate and ammonium chloride be ball-milled together, as such a mixture causes much less fuming. The authors have found, however, that in addition to reducing the fuming, the two constituents become so intimately admixed by such a process that they exert a very much stronger disintegrating action than mixtures ground by hand in a mortar. The mixture is prepared by adding one part of resublimed ammonium chloride to eight parts of precipitated and washed calcium carbonate, and is ball-milled in a porcelain mill for 5 hours with flint balls. Although Hillebrand and Lundell (*10*) assert that the calcium carbonate should be kept by itself, and not mixed with the ammonium chloride, the ball-milled mixture is made up in the Norton laboratories and stored in large batches; it is just as effective and has the same blank after standing 12 months as when freshly prepared. Lundell, Hoffman, and Bright (*12*) now recommend this procedure.

The sample to be fused is thoroughly mixed by hand with nine parts of the ball-milled preparation, and is placed in the crucible directly, without any bottom or top layer of calcium carbonate; no loss is occasioned by omitting these "protecting" layers, even at the high temperature employed. This procedure has the further advantage that the leaching process after fusion is much more readily effected.

It is asserted by most authorities that complete solution of the residue in hydrochloric acid after leaching is conclusive proof that complete decomposition has been effected by the fusion. This statement must not be accepted too literally, because solution of the residue in acid cannot prove more than that decomposition has proceeded to a certain point. In many cases where the residue is completely soluble in acid it still retains tenaciously some alkali that cannot be leached out with water (*9, 13, 17*); spectrographic checks on the residues have confirmed these observations. The modifications of the J. L. Smith fusion suggested above reduce to a minimum this tendency of the residues to retain alkalies, but no fusion or leach should be considered complete until elementary precautions have been taken to ascertain that it is.

The above-mentioned considerations explain why so many analyses yield results lower than the true alkali values. In a careful analysis high results are seldom obtained, and if obtained are usually due to incomplete removal of calcium, to carelessly conducted blank determinations, and particularly to failure to provide for the removal of magnesium. Every text on the subject that the authors have seen states that the chief advantage of the J. L. Smith fusion is the elimination of magnesium from the start; while they repeat this statement (*10*), Hillebrand and Lundell nevertheless recognize elsewhere (*2, 11*) its inaccuracy and make provision for the magnesium that usually accompanies the alkalies, without, however, attaching to their proviso the importance it deserves. Magnesium will usually be found even in the blanks, and too much emphasis cannot be laid on the necessity of correcting the final weight of the alkali chlorides for it.

Analysis of Beta-Alumina

Perhaps the most interesting application of these modifications of the J. L. Smith fusion to a difficultly attackable substance is the analysis of so-called beta-alumina. This was prepared and described by Rankin and Merwin (*16*), analyzed for them by Washington (*19*), and was asserted to be entirely Al_2O_3 and therefore an allotropic modification of aluminum oxide. The authors have since found that beta-alumina can be prepared only if the aluminum oxide used contains sodium, and that beta-alumina is probably a sodium aluminate because it contains 4.82 per cent Na_2O. Table I shows a comparison of the analytical results obtained on typical specimens of this substance using the authors' modifications of the J. L. Smith fusion, and the results obtained by others, most of whom secured their samples of beta-alumina from the authors; detailed reasons for believing that this beta-alumina is really a sodium aluminate are being published elsewhere.

Table I. Sodium Content of Beta-Alumina

Sample No.	Na_2O	Al_2O_3	Analyst
	%	%	
1	..	100	Washington (*19*)
2	..	100	R. Dalton for Hendricks and Pauling (*7, 21*)
3	2.56	....	H. Swanson for Gallup (*5*)
4	2.56	96.59[a]	E. Spuhrmann for Gottfried (*6*)
5	4.59	95.30[b]	Norton Co.
6	4.76	....	Norton Co.
7	4.87	....	Norton Co.

[a] Contains small amounts of other impurities.
[b] Contains small amounts of other impurities; sample was somewhat decomposed by acid treatment before analysis.

The only method other than Smith's for determining the alkali content of insoluble materials is that of Berzelius (*1*); but, if a material is not completely decomposable in acids, this method obviously fails. Alkalies are strongly adsorbed and tenaciously retained by many compounds, so any leaching process that does not afford complete decomposition of the sample cannot be accurate; if the alkali is present combined as a compound, there is no possibility of leaching it out

without previous decomposition. These considerations may explain some of the discrepancies in the amounts of sodium found by different analysts in beta-alumina, listed in Table I. In some cases the J. L. Smith procedure was not employed.

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Occurrence of Selenium in the Colorado River and Some of Its Tributaries

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DURING the past few years the writers have been engaged upon an investigation of the occurrence of selenium in soils (*1*). In the fall of 1934, W. D. Collins, of the Quality of Water Division, U. S. Geological Survey, kindly furnished a composite sample of water from the Colorado and Gunnison rivers in western Colorado. This was found to contain 0.015 part per million of selenium. As a result, C. S. Howard, of the same division, in December, 1934, collected a series of water samples from the same area, as well as a series of soil incrustations. In the spring (May, 1935) C. S. Howard, John T. Miller, and H. G. Byers collected a further series of samples of soils and water.

The samples collected have been analyzed by K. T. Williams. The methods employed were essentially those described by Robinson and others (*2*). The results obtained are given below in tabular form. Table I contains the data concerned with the water samples themselves and Table II the analyses of certain soils and soil incrustations which emphasize the conclusions reached concerning the sources of the selenium.

TABLE I. SELENIUM CONTENT OF WATER SAMPLES FROM COLORADO RIVER AND RELATED SOURCES

Lab. No.	Field No.	Location	Selenium
			P. p. m.
B14417	1	Colorado River near Cameo	0.000
14423	8	Gunnison River near Cimarron	0.000
15197	3	Uncompahgre River 5 miles south of Ouray	0.000
15196	2	Uncompahgre River 13 miles south of Colona	0.000
15198	4	Bear Creek 3 miles south of Ouray	0.000
15200	6	Cow Creek at Highway Bridge	0.002
15201	7	Uncompahgre River at Colona (1935)	0.002
14422	7	Uncompahgre River at Colona (1934)	0.003
14425	10	Uncompahgre River 0.75 mile west of Delta	0.220
14427	12	Gunnison River 0.5 mile north of Delta	0.007
14420	4	Gunnison River near Redlands	0.080
14420A	5	Colorado River near Grand Junction	0.030
	31	Dolores River near Cisco, Utah	Trace
	32	Green River at Green River, Utah	Trace
	33	Colorado River near Topock, Ariz.	0.030
14421	6	Drainage ditch in Montrose	0.700
14426	11	Relief drainage ditch, 2 miles east of Delta	0.320
14424	9	Main lateral 1 mile south of Chipeta	1.050
14419	3	Main drain 1.5 miles east of Loma	0.630
15203	9	Surface drainage 1 mile north of Mack	0.007
15204	10	Surface drainage near Loma	0.003
14418	2	New drain 4 miles north of Mack (1934)	1.980
15202	8	New drain 4 miles north of Mack (1935)	2.680

The data of Tables I and II are of interest not only because of the demonstration of the presence of selenium in river water, a fact not heretofore recorded, but because they indicate very clearly the sources of the selenium found. The Colorado river water is diverted near Cameo, Colo., to irrigate a large tract of land in the vicinity of Grand Junction in Mesa County. The Gunnison water is diverted near Cimarron, Colo., to provide a portion of the water used on the Uncompahgre irrigation project in Montrose and Delta Counties. The Uncompahgre river water is diverted near Colona for the same project. Examination of the data in Table I (Field Nos. 1, 7, and 8) reveals the fact that at these diversion points the Colorado and Gunnison contain no selenium, at least none in excess of one part per billion. The Uncompahgre at Colona, however, contained 3 parts per billion in December, 1934, and 2 parts per billion in May, 1935. These streams receive the surplus irrigation water as well as the surface and subsurface drainage water at points further down the streams. The Gunnison river near Delta, at the lower end of the Uncompahgre irrigation tract, has a selenium content of 0.007 part per million. Near its point of junction with the Colorado, after receiving drainage from the irrigated area near Whitewater and a part of the Grand Junction tract, its selenium content has increased more than tenfold. The Uncompahgre, near its mouth at Delta, has increased its selenium seventy-fold over that at Colona. The Colorado has no selenium until it receives drainage from the irrigated area, but at Grand Junction it has a selenium content of 30 parts per billion. The other tributaries of the Colorado examined contain negligible quantities of selenium, but it seems evident that sources other than the Gunnison exist, since otherwise dilution would have decreased the selenium content by the time Topock, Ariz., is reached. The selenium content of the Uncompahgre at Colona is 2 parts per billion, and is zero above the mouth of Cow Creek, and between Cow Creek and Colona there is a fairly large irrigated area. Whether any irrigation is practiced along Cow Creek is not known to the writers.

That the chief source of selenium is the drainage of the

Table II. Selenium Content of Soils and Soil Incrustations in the Vicinity of Montrose and Grand Junction, Colo.

Lab. No.	Field No.	Location	Material	Selenium *P. p. m.*
B14412	18	Near main lateral 1 mile south of Chipeta (near B14424, Table I)	Salt crust	100.0
14413	19	Near main lateral 1 mile south of Chipeta (near B14424, Table I)	Ooze in ditch	4.0
14414	20	Bar in Uncompahgre River (near B14425, Table I)	Sandy clay	9.0
14415	21	Relief drainage ditch, 1 mile east of Delta (near B14426, Table I)	Ditch deposit	28.0
14416	22	Drainage ditch (near B14427, Table I)	Ditch deposit	1.5
14442	28	Main drain 1.5 miles east of Loma (near B14419, Table I)	Salt crust	16.0
14439	25	6.5 miles east of Fruita	Salt crust	260.0
15003	2	6 miles east of Montrose, Montrose County	Clay soil 0–6 inch	3.5
15022	8	2.5 miles east of Montrose, Montrose County	Gypsiferous shale	3.5
15054	4	Sec. 26, T.15 S, R.95 W., Delta County	Chipeta clay 0–12 inch	3.0
15060	5	Sec. 19, T.15 S., R.95 W., Delta County	Billings clay 0–12 inch	4.0
15075	1	Sec. 10, T.9 S., R.103 W., Mesa County	Billings clay loam 0–12 inch	2.0
15078	1	Sec. 10, T.9 S., R.103 W., Mesa County	Billings clay loam 36–48 inch	8.0
15079	2	Sec. 15, T.9 S., R.103 W., Mesa County	Billings clay loam 0–12 inch	2.0
15082	2	Sec. 15, T.9 S., R.103 W., Mesa County	Billings clay loam 36–48 inch	5.0
B15085	4	Sec. 15, T.9 S., R.103 W., Mesa County	Alkali crust	52.0
15102	13	1.25 miles east of White Water	Billings clay loam 0–12 inch	3.0
12104	M27x	4.5 miles north of Loma, Mesa County	Mancos shale	2.0
12109	M27x	5.5 miles north of Loma, Mesa County	Mancos shale	6.0
15022	8	2.5 miles east of Montrose, Montrose County	Gypsiferous shale	3.5
15065	5	8 miles north of Delta, Delta County	Mancos shale	2.0

irrigated lands is made clearly evident by the data on the drainage waters examined. All the drainage waters examined from this section of Colorado contain selenium. The most striking examples are furnished by Nos. B14421 and B14424, both in the Uncompahgre area, and by B14419 and B14418, both in the Grand Junction area. The source of the selenium in the drainage water is clearly evident through consideration of the data of Table II. On the banks of the drainage ditches occur salt incrustations and these are in effect seepage deposits. They range in selenium content from 16 to 260 parts per million. Even the ooze (B14413 and B14416, Table II) in the ditches has a selenium content, and also a mud bar in the Uncompahgre river (B14414).

The soils of the whole area concerned in this investigation are derived from shales which contain selenium. The selenium content of representative shales is shown in Table II by Nos. B12104, B12109, B15022, and B15065. The quantity found in the soils varies considerably over the area. A few examples only are given in Table II.

Of special interest are samples B15075, B15078, B15079, B15082, and B15085 of Table II because of their relation to samples B14418 and B15202 of Table I. The new drainage ditch 4 miles north of Mack was sampled by C. S. Howard only a few weeks after its completion and before any great amount of drainage had taken place. It was sampled again after it had been in operation for about 6 months, when it was delivering a small flow of water. The water it contained was seepage through the soil, represented by samples B15079 and B15082 (Table II). The nonirrigated area adjacent to it is represented by samples B15075 and B15078 (Table II). Sample B15085 is a seepage incrustation near the ditch.

These observations have a practical aspect aside from their scientific interest, in that they indicate clearly the possibility of improvement of seleniferous land by irrigation and drainage where such management is practicable.

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Semi-Micro-Kjeldahl Determination of Nitro and Azo Nitrogen

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SEMI-MICRO adaptations of the classical Kjeldahl method, suitable for the estimation of nitrogen in combination as amine, amide, or imide, have been reported by Hitchcock and Belden (*3*) and Northrop (*4*). By modifying the method of Elek and Sobotka (*2*) for the determination of nitro nitrogen in micro- and macrosamples, a successful technic for the estimation of nitro and azo nitrogen on the semimicro scale has been devised.

Procedure

An accurately weighed sample of the dried substance, to contain from 2 to 5 mg. of nitrogen, is introduced into a dry 100-ml. Kjeldahl flask having a constriction about halfway up the neck, avoiding, as far as possible, deposition on the neck of the flask. Three hundred milligrams of c. p. dextrose, 1 to 1.5 grams of potassium sulfate, about 20 mg. of small copper sulfate crystals, and a few bits of well washed alundum (grain size 14, boiled out 5 to 6 times with distilled water until the washings showed no change of pH), are added to the flask whose neck is then washed down with 4 ml. of concentrated sulfuric acid (sp. gr. 1.84), care being taken to leave the neck entirely free of adhering particles. The mixture is digested over a shielded microburner with the flask in a nearly horizontal position, the heat being applied through a 2.5-cm. (1-inch) hole in an asbestos board. As soon as the digestion mixture has become homogeneous one drop of selenium oxychloride is added. Heating is continued until the solution is clear and for 15 to 20 minutes thereafter. The time of digestion varies from 35 to 45 minutes.

To the cooled solution 35 ml. of distilled water are added, and, just before distillation, the solution is made alkaline with 12 ml. of a clear 50 per cent sodium hydroxide solution, in the usual fashion. The distillation apparatus is the same as that described by Hitchcock and Belden (*3*). The distillate is received in 25 ml. of 0.02 *N* hydrochloric acid, and the excess acid is titrated with 0.02 *N* barium hydroxide, using as indicator the mixture of methyl red and methylene blue described by Andersen and Jensen (*1*). Blank values on the reagents vary from 0.10 to 0.20 ml. of 0.02 *N* solution. Typical analytical data are shown in Table I.

Table I. Semi-Micro-Kjeldahl Determination of Nitro and Azo Nitrogen

Substance	Weight of Sample	Nitrogen Found		Theory
	Mg.	*Mg.*	%	%
p-Nitroaniline, Kahlbaum	20.4	4.13	20.2	20.29
	20.4	4.14	20.3	
p-Aminoazobenzene, Kahlbaum	23.1	4.90	21.2	21.32
	22.5	4.78	21.2	
3-Nitro-5-carboxyphenylglycyl sulfanilic acid	21.8	2.30	10.5	10.63
3-Nitro-5-carboxyphenylglycyl aniline	23.6	3.11	13.2	13.33
Helianthine	19.9	2.72	13.7	13.77
	19.8	2.72	13.7	
Benzeneazoresorcinol	26.5	3.44	13.0	13.08
p-Nitromalanilic acid	30.8	3.38	11.0	11.02
p-Nitrobenzoyl tyrosine ethyl ester	24.3	1.88	7.8	7.83

It is extremely important that the flask be thoroughly dried before the sample is introduced, since the presence of more than the traces of moisture contained in the reagents causes excessive foaming which prevents satisfactory completion of the digestion.

The method described permits of economy of time and substance with retention of a high degree of accuracy and precision. It has been used for more than a year for the routine analysis of new preparations with continued satisfaction. No special balance is required, a fine analytical balance being completely adequate.

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Continuous Production of Distilled Water Free from Carbon Dioxide and Ammonia

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THIS laboratory was recently faced with the necessity of continuously producing high-grade distilled water free from ammonia and carbon dioxide and having a specific conductance of 0.5×10^{-6} mho. or less. Tap water and steam were available (Tables I and II). When tap water was used in a hardwater type of Barnstead gas-fired still the best distillate obtained had a specific conductance of 5.0×10^{-6} mho. This was obtained with very little bleeding through a continuous overflow and with the condenser venting free steam.

Table I. Analysis of Tap Water Available

	P. p. m.
SiO_2	14.1
Ca	66.9
Mg	31.4
NH_3	5.3
Na	34.8
SO_4	1.2
Cl	4.0
Alkalinity: phenolphthalein, 0; methyl orange	37.6

Table II. Analysis of Condensed Steam

	Condensate Leaving Condenser	
	At 20° C.[a]	At 100° C.[b]
CO_2, p. p. m.	9 to 16	0.7 to 1.0
NH_3, p. p. m.	10 to 12	
pH	6.0 to 6.5	8.0 to 9.0

[a] Specific conductance 16.6×10^{-6} to 12.5×10^{-6} mho.
[b] Specific conductance 6.6×10^{-6} mho.

The conductance was determined by passing a small amount of the distilled water through a totally enclosed type of conductivity cell. The resistance was determined by means of a dial type of Wheatstone bridge and a pointer type of alternating current galvanometer using 60-cycle current. The cell constant was about 20. The water leaving the still passed through a tin pipe.

The still was rearranged so that condensed steam from the steam heating system was used as make-up to the still, but again the best distillate produced had a specific conductance of 5.0×10^{-6} mho. The still was modified so that air, free from carbon dioxide and ammonia, could be added just below the water level and passed through the condenser with the condensing steam. The quality of the distillate remained the same and it was found to contain no carbon dioxide but appreciable amounts of ammonia.

The condenser used to condense the steam from the steam-heating system was then modified so that the condensate left the condenser at 100° C. with appreciable amounts of uncondensed steam flashing to the atmosphere. Table II shows the composition of the condensate after being collected in this manner. The carbon dioxide was low, but the ammonia had not been materially reduced. With such water being fed to the still, the ammonia would be carried with the steam and remain in the distillate. Tests were then run after continuously adding various amounts of sulfuric acid mixed with sodium dichromate to the condensed steam being fed to the still and with the still arranged so that a constant level was maintained by an overflow (Figure 1). When no air was being fed to the still the distillate from the still had a conductance of 1.0×10^{-6} mho. and

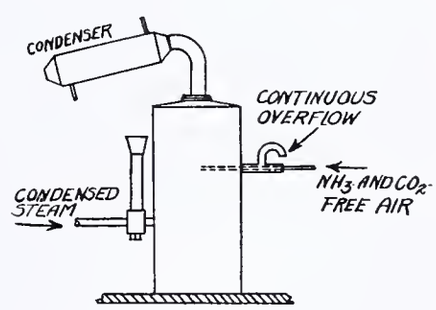

Figure 1. Modified Still

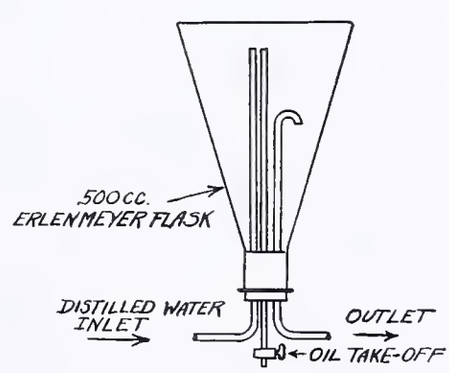

Figure 2. Oil Separator

a pH value (using a glass electrode) of 6.0. When air free from ammonia and carbon dioxide was blown through the still, the conductance changed to between 0.5×10^{-6} and 0.3×10^{-6} mho. with a pH value of 6.8. Variation of the acid feed showed that the best results were obtained when the pH value of the overflow water from the still was around 3.5.

After running with this type of treatment for several months, the still was found to be in very good condition. A black coating appeared below the water level but the tin coating was still intact beneath it.

A typical balance of acid feed and distilled water generated is as follows: The acid chromate solution was made up with 9 cc. of concentrated sulfuric acid and 10 grams of sodium chromate to 5 liters of water. This was added by means of a continuous feeding device at the rate of 30 cc. per minute. About 15 liters per hour of condensed steam were mixed with the acid feed and fed to the still, the excess above the amount distilled overflowing to waste. Nine liters per hour of distilled water were generated. The water overflowing from the still had a pH value of about 3.5.

The steam from the heating system contained a small amount of oil, giving a faint opalescence to the condensed steam, but the distillate from the still was perfectly clear. The oil appeared to carry over and deposit in the tin piping and from time to time globules of oil about 0.16 cm. in diameter came through with the water. A separator shown in Figure 2 was installed. The oil collected on the top of the solution and was drawn off through a valve, so that the resulting water was free from oil.

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A Precision Oil Gage

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INCREASING application of vacuum practice to fractional distillation has stimulated the development of a variety of pressure control devices (*2, 3, 5, 6*). Marked progress in this direction has been made in recent years, and control devices capable of a high order of precision have been developed (*3, 6*). Progress has lagged, however, in the development of gages capable of measuring the small pressure changes often involved—changes of a magnitude comparable with the precision control now possible by the improved devices.

The ordinary mercury manometer of the U-tube type, the most widely used in laboratory practice, permits a wide range of absolute pressure measurements but is comparatively coarse and insensitive. Pressure changes less than 0.25 mm. cannot be read with any reasonable degree of accuracy.

As may be observed from vapor pressure curves generally, there is a marked decrease in pressure per unit of temperature as one approaches the low pressure region. Temperature changes in the higher pressure regions generally conform to relatively marked changes in pressure and are not apt to be confusing. But at 20 mm. or under, a temperature change of 0.2° and sometimes more in a distillation may be due to pressure changes (in the system) which cannot be detected on the manometer rather than to any change in composition of the vapors—the inference usually drawn.

An urgent need therefore exists for pressure gages of high precision, particularly in the range of 40 mm. or less.

The McLeod gage, useful in high-vacuum work, has a limited usefulness in this field since it provides a very narrow range, necessitates separate manipulation for each observation, requires tedious calibration, and cannot be used with condensable gases.

A mercury gage developed by Dubrovin (*1*) intended to fill this need, has a pressure range up to 20 mm. and permits a magnified reading of about 9 to 1, but the magnification is not uniform over the 20-mm. range, so that for precision work calibration throughout the entire range is here also necessary. In addition, reconditioning of the gage, occasionally required, makes recalibration necessary after each reconditioning.

A sensitive U-manometer constructed of large diameter tubing and utilizing sulfuric acid as the manometric liquid was described in a previous publication (*6*). One millimeter on this manometer is equivalent to less than 0.125 mm. of mercury. The high absorptive capacity of strong sulfuric acid for olefin, terpene, and other unsaturated vapors, however, renders this manometer, in the course of time, unreliable when used in distillations involving these compounds. Even with efficient trapping devices, occasionally "reboiling" out of this instrument becomes necessary.

Oil Gages

The magnified reading and consequent increased precision that is possible with light liquids such as butylphthalate has long been recognized. But, as is well known, these liquids can only be used in the U-type manometers of the open-arm form, such as the Hickman gage (*4*), because of the impossibility of dislodging the liquid from the closed end. To provide the necessary reference vacuum, therefore, the Hickman gage utilizes a butylphthalate condensation pump as an integral part of the gage assembly. Its operation is necessarily a continuous function of the gage while the latter is in use.

In this paper, an improved gage is described which utilizes oil or other light nonvolatile medium as the manometric liquid and does not require a high-vacuum condensation pump for either its preparation or its use. For purposes of preparing or conditioning the gage a good laboratory pump, usually the same one used in connection with the vacuum distillation, is sufficient. After that, it functions much like any other type of gage, independent of the pump. Production of a reference vacuum, comparable to the Torricellian vacuum of the ordinary U-tube type, is made possible primarily by the construction of the gage.

With reasonable safeguards, the reference vacuum can be maintained for a long time and the gage can be used either continuously or intermittently without the need for reconditioning, although conditioning is, in itself, a very simple process and can be repeated for checking purposes as often as desired.

With paraffin oil as a manometric liquid, a pressure difference of 1 mm. oil level is equivalent to less than 0.067 mm. of mercury. Assuming an accurate reading of 0.5 (mm.) division, pressure changes of 0.033 mm. of mercury may therefore be read with precision. The oil level is, furthermore, very responsive to small pressure changes, no tapping, etc., as in mercury manometers, being required.

The gage is in effect a double U-tube type manometer in which both oil and mercury are employed, the latter serving, however, only as a mobile "backing" medium for the oil column.

Reservoirs 30, 31, and 32 are joined hermetically, as indicated, by thick-walled capillary tubes of approximately 1.5-mm. bore for the tube between reservoirs 30 and 31, and 2.5 mm. between reservoirs 31 and 32. Reservoir 30 serves as the mercury reservoir, 32 as the oil, and 31 as a temporary common reservoir for both, also as a degassing chamber and as a space for the Torricellian vacuum, comparable to the closed end of the simple U-type mercury manometer.

Stopcocks 33 and 34 directly below reservoirs 30 and 32, respectively, serve to lock the two liquids, mercury and oil, as necessary. The three-way stopcocks, 35 and 36, serve primarily to establish communication with the pumping system, the atmosphere, or the system whose pressure is to be measured, and for manipulating the movement of the liquid during preparation for use as explained below.

The three-way stopcock, 37, provides a means for selective communication either directly with the pumping system or with the gas system whose pressure is to be measured, as the case may be. The relative position of the reservoirs, their dimensions, etc., are in general as indicated in the illustration. The position of 30 must, however, be such as to insure against a differential mercury height in excess of 76 cm. (barometric height), so as to make possible free movement of the mercury through the whole apparatus when so desired. Thus, the greater the oil reading range desired, the higher the mercury reservoir 30 must be set up.

In order to maintain a Torricellian reference vacuum, the oil or other light liquid must be suitable for manometric work, have a very low vapor pressure and reasonably low viscosity, and be free from volatile impurities, to insure against the filling of reservoir 31 with vapors.

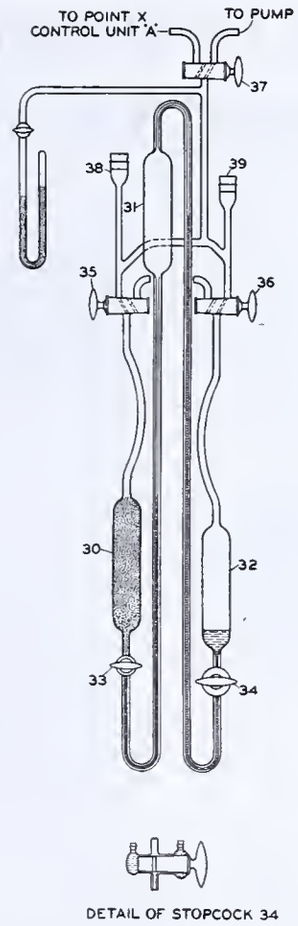

FIGURE 1. DIAGRAM OF GAGE

Conditioning Gage for Use

The requisite quantity of purified mercury is introduced into reservoir 30 by way of opening 38 (ordinarily kept closed with rubber stopper) and stopcock 35 by applying slight suction through 37 and is allowed to fill the capillary tube up to bottom of reservoir 31. The mercury is then locked in position by stopcock 33. The rest of the system (reservoirs 31, 32, capillary, etc.) is then evacuated by communication with the pump by way of stopcocks 34, 36, and 37. Stopcock 36 is then locked and the requisite quantity of oil or other nonvolatile manometric liquid is introduced through opening 39 and drawn into reservoir 32 through stopcock 36 and thence into reservoir 31. By proper manipulation of appropriate stopcocks the mercury layer and its overlying oil layer are then allowed to rise in reservoir 31 to a point about one-half or two-thirds full. Stopcock 33 is then locked. Suction is applied to both sides of the system by way of the pump and pumping continued until no further gas evolution is evident. Heat may be applied to hasten the degassing process. Reservoir 30 is then opened to the atmosphere by way of stopcock 35 and by careful manipulation of stopcock 33, mercury and oil are pushed upward, the oil layer being sent through the capillary and the major part into reservoir 32 until the top of the mercury column is at the top of reservoir 31. The oil layer is then locked by stopcock 34 and, with the pump operating continuously, the three-way stopcock is turned to evacuate reservoir 30. When the pressure has been sufficiently lowered, the mercury thread will break at the mercury-oil juncture and the mercury column is then allowed to drop and empty reservoir 31. Stopcock 33 is then locked. There is thus produced a Torricellian vacuum between the mercury and oil. Moreover, since reservoir 31 is relatively large, the effect of any trace of residual gas in the mercury or oil that had not been removed in the degassing process is so minimized as to constitute a negligible factor. With the pump operating continuously, stopcock 34 is now opened, the oil column drawn over to a convenient level, locked again by 34, and is now ready for use. Communication with the system to be measured is made through stopcock 37. Stopcock 34 is opened and differential pressure read directly as in the ordinary mercury U-type manometer.

SPECIAL STOPCOCK 34. While any well-ground, long-barreled stopcock can be used, the mercury-sealed, or grease-sealed stopcock (shown in detail) is preferred. The grease should be "high vac" type, free from volatile matter.

The bores, respectively, of the tube below the stopcock, the plug, and the tube above the stopcock are progressively larger, as shown, in order to prevent the trapping of air bubbles.

Some indication may be had of the uniformity of behavior of the oil gage throughout its pressure range from the data in Table I. Comparative readings were made with the oil gage and a well-made simple U-type mercury manometer, using the pressure control unit (described in another paper, *6*) to maintain constant pressure at the various points while making the observations. Readings were checked by T. H. Harris of this laboratory.

The mercury gage could probably be read at best to a fourth of a division (0.25 mm.).

The values given in column 3 of Table I were obtained by dividing the oil readings by 15.53, the ratio of the specific gravities of mercury and oil.

It was found that pressure readings could be made more rapidly and accurately by using the top of the wide meniscus (reservoir 32) for the 0 reference point and reading the distance between it and the bottom of the meniscus in the capillary rather than reading the distance between the bottom of the two menisci. The difference between top and bottom should, however, be determined as also the error due to capillarity. The latter is best determined on a separate piece of capillary tubing (2.5 mm.). These errors are compensating and their difference, which is generally within 1 mm. of oil (0.06 mm. of mercury), is applied as a correction for absolute pressure reading.

TABLE I. COMPARATIVE READINGS

Reading on Oil Gage[a]	Reading on Hg U-Manometer[b]	Oil Reading Calculated[c] to Mm. Hg
Mm.	*Mm.*	
543	35	34.97
544	35	35.04
308.5	19.8	19.86
296	19+	19.06
155	10−	9.91
136	9−	8.76
82.5	5.3	5.31
29	2−	1.87
311	20	20.03
297	19+	19.12
233	15.2	15.03
155	10.0	9.91
77.2	5.0	4.97
25.5	1.7	1.64

[a] Oil used was Apiezon-B (J. Biddle and Co., Philadelphia), sp. gr. 0.8712 at 25/25°.
[b] Mercury manometer readings accurate to about 0.3 mm.
[c] Calculated values obtained by dividing oil readings by 15.53—the ratio of the specific gravity of mercury to that of the oil.

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Improvements in Design of Pressure Control Assembly

S. PALKIN, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

IN A PREVIOUS publication (*2*) a design embodying a dual system of pressure control was described. In the new design shown in Figure 1 the control apparatus has been improved and its operation simplified, thus permitting better coördination with the distillation apparatus. For detailed measurements and construction of the essential parts of the control assembly, the reader is referred to the previous publication (*2*).

The low-pressure system both for the main control unit, *A*, and for the auxiliary unit, *C*, is indicated in the drawing by heavy dark lines. Both barometric and short U-tube type manometers are used in order to provide full range of pressure up to atmospheric and are distributed in various parts of the apparatus as shown, so that pressure in all parts of the assembly, including the auxiliary units, may be observed at any time.

The arrangement has been so simplified that after taking a fraction of distillate from 4 and locking stopcocks 5 and *S*, reevacuation of 4 is accomplished with the manipulation of but two stopcocks—*S* of the control unit and 5 of the distillate reservoirs. This is done as follows: Three-way stopcock *S* is opened to reservoir 4. The pump, thus automatically started by mercury manostat *V* and relay *r*, exhausts reservoir 4 and when the proper pressure (equal to the distillation pressure) has been reached, as indicated by manometer t_1 or t_2, stopcock *S* is turned back to its original position, open to low-pressure flask *K*, and stopcock 5 is opened to 6, bringing it back in communication with the column distillation system. No other manipulations are necessary, as all other operations are taken care of automatically.

The same simplicity of manipulation in taking a fraction holds for a battery of stills operated at the same time where all are run at the same pressure.

Where simultaneous operation of several pieces of apparatus requires pressures differing from one another, smaller auxiliary control units as shown in *C* may be joined to the assembly. Such auxiliary units do not possess the high degree of precision possible with the sulfuric acid manostat (*1*), but have been used satisfactorily, for example, for controlling the temperature of a column still jacket and for an Abderhalden drying apparatus. Here the desired temperature is obtained by boiling a suitable liquid at a set pressure controlled by the auxiliary unit.

The auxiliary unit is similar to the large unit, *A*, but simpler and consists of a capillary valve–manometer mechanism (set in the large test tube, 20) and a mercury manostat, 21. The magnet operating the valve receives the current from a 110-volt circuit (d. c.) in series with a 7.5-watt lamp, 22, which provides the necessary resistance. The mercury manostat, 21, acts both as a manostat and a switch, thus obviating the need for a relay. Stopcock 23 serves as a by-pass. Capillary stopcock 24 provides connection with the atmosphere when necessary.

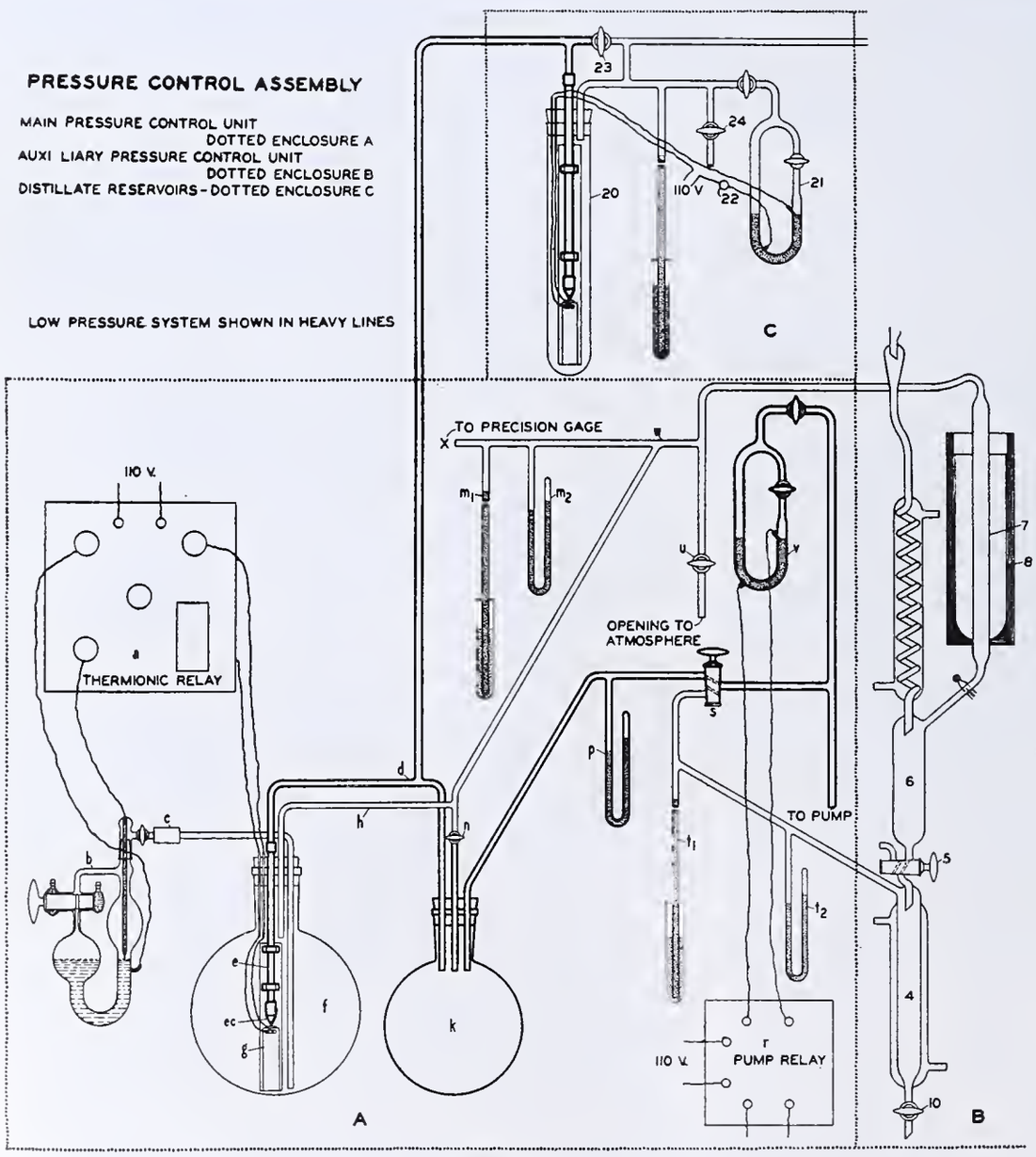

FIGURE 1

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RECEIVED July 15, 1935. Presented before the Division of Agricultural and Food Chemistry at the 90th Meeting of the American Chemical Society, San Francisco, Calif., August 19 to 23, 1935.

A Convenient Absorption and Titration Flask for Carbon Dioxide Determination

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A PRECISE method of determining carbon dioxide in air has been described by Thomas (*2*). A modified form of the absorption unit described, which has been found very useful for a variety of carbon dioxide determinations, consists of a 250-cc. Erlenmeyer flask with a side arm drawn down at the end for tube connection and a fritted glass disk sealed in the tube at the point where it begins to taper. The flask was made by blowing a hole in the end of a test tube, sealing on a small piece of tubing, and fusing a porous disk at *A* (Figure 1). The tube was then sealed into the side of the flask. The disk was made of 100- to 200-mesh glass and was prepared by the method described by Bruce and Bent (*1*).

To operate, 25 to 50 cc. of the absorbing solution with a few drops of normal butyl alcohol are placed in the flask, the side arm is attached by a rubber connection to the source of gas to be analyzed, and suction applied through a tube in the stopper. As soon as suction is applied, the flask is rotated so that the side arm is nearly vertical. Before the suction is removed and the pressure equalized, the side arm is brought to a horizontal position to prevent liquid passing through the disk. The contents are titrated through a tube in the stopper. For precise work, carbon dioxide is removed before starting a determination by filling with water and then replacing the water with carbon dioxide–free air through the side arm. Usually, a correction for the initial carbon dioxide in the flask, made from a blank determination, is sufficiently accurate.

Tenth normal sodium hydroxide is satisfactory as an absorbing solution. When absorption is complete, an excess of 10 per cent barium chloride solution is added through a tube in the stopper and the excess base titrated against 0.1 *N* hydrochloric acid. It is necessary to clean the porous disk occasionally with hydrochloric acid to prevent clogging with barium carbonate. The contents of the flask may be protected from contact with outside air by introducing all solutions through a rubber tube in the stopper, which is kept closed by a clamp except while the solutions are being introduced. Barium hydroxide is not suitable for an absorbent if much carbon dioxide is present, because the barium carbonate clogs the pores in the disk, but barium chloride may be added before titration.

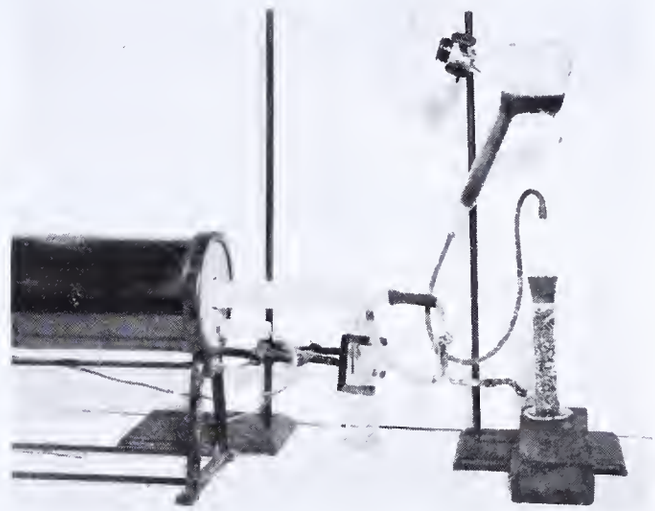

FIGURE 3. ASSEMBLY FOR DETERMINING TOTAL CARBON

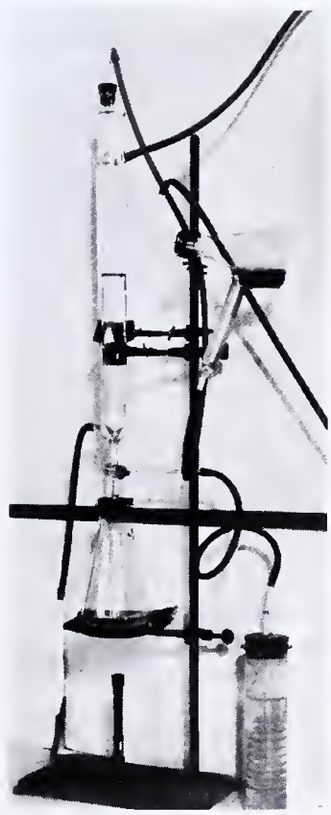

FIGURE 2. APPARATUS IN OPERATION

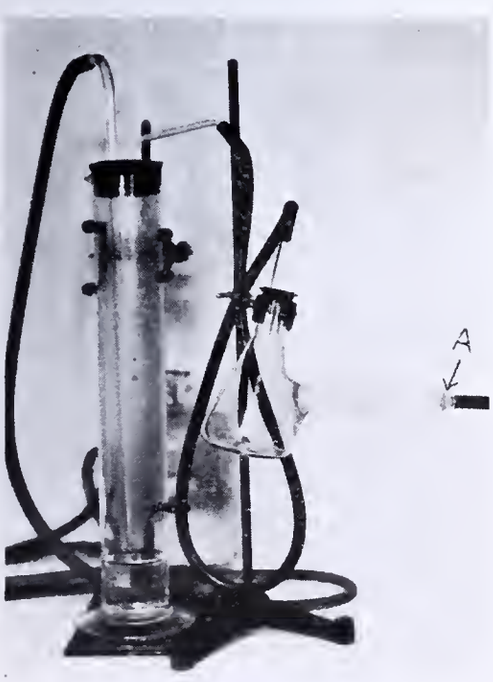

FIGURE 1. ASSEMBLED EQUIPMENT

The equipment as assembled in Figure 1 has been used to determine carbon dioxide in the soil air and to measure the concentration of carbon dioxide in desiccators over a number of materials, including soil and cereals. When measuring carbon dioxide in the soil air, the side arm was connected directly to a tube inserted into the soil.

The device has been found very convenient in determining the carbonate and total carbon content of soils, particularly where the carbon content is low. Figure 2 shows the carbonate apparatus in operation.

The sample to be analyzed for carbonate is weighed into a wide-mouthed Erlenmeyer flask which is connected to a source of carbon dioxide–free air and through a condenser to the side arm of the absorber. Suction is applied by an aspirator pump. Acid is added to the soil through a large buret and the rate of gas flow regulated by the pump.

Total carbon may be determined conveniently by connecting the flask as shown in Figure 3, instead of the usual absorption train, to a combustion tube containing the sample. Titrating the contents of the flask takes no more time than weighing the absorption bulbs and is more accurate for small amounts of carbon. When determining total carbon in soil the sample is mixed intimately with manganese dioxide in a boat and placed in a combustion tube in the furnace. The gases from the tube pass through an absorber containing granular zinc to remove acids from the oxidation of sulfur and nitrogen compounds, through a sulfuric acid bulb (not shown in the figure, usually may be dispensed with) to remove any ammonia, and then to the carbon dioxide absorption flask. A stream of carbon dioxide–free oxygen is passed through the system during the determination and the furnace is run at about 900° C. About 10 minutes are required for a determination.

If the method is to be used for determining carbon in a variety of compounds, the chain preceding the carbon dioxide absorber would depend, of course, upon the composition of the material being studied. The zinc absorber does not remove nitric acid completely, but the error resulting is usually small with soils and, if necessary, can be corrected by a nitrate determination of the residue in the flask after titrating.

The extremely small bubbles produced by the porous glass disk when the surface tension of the absorbing liquid has been lowered with a higher alcohol make absorption very rapid. The author's results confirm the data presented by Thomas (*2*) which show that several hundred milliliters of air per minute can be passed through this type of absorber and still get very high absorption.

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Received June 26, 1935.

Recent Developments in Platinum Thermocouples

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With the use of the National Bureau of Standards 1933 reference tables (*3*) for platinum to platinum-rhodium thermocouples, the deviation curves obtained for individual couples have no points of inflection and are mostly linear. The improvement in these tables over those previously used is found principally at the higher temperatures, and particularly above 1200° C. (2200° F.). The accuracy of temperature measurements obtainable with such couples is now limited by the quality of the thermocouple wires and (unless corrections based upon an individual calibration of the actual couple used are applied to each reading) upon the limits within which the manufacturer can keep the deviations of the e. m. f. of his couples from the standard values. This situation seemed to make closer tolerances desirable.

In the past few years definite improvements have been made in the manufacture of platinum-rhodium thermocouples, increasing their effective life, their resistance to deterioration at high temperature, their homogeneity, and their reproducibility. The following data are presented to indicate what tolerances it is possible for a manufacturer of rare metal thermocouple wire to meet.

In 1934, this company adopted shop specifications with tolerances much closer than had ever been used for platinum and platinum-rhodium, and has been able to adhere rigidly to these specifications. While they may not represent the ultimate tolerances which might be met in special cases, they are significant in that they indicate the quality (as demonstrated by actual experience) which a manufacturer may be reasonably asked to maintain in the general run of his product.

General Considerations

Since the first effect in service is, in general, a lowering of the e. m. f. of a platinum-rhodium thermocouple, it is obvious that a couple which originally yields an e. m. f. lower than the standard will, in service, gradually depart further. It is, therefore, important to allow only positive deviations from the standard (N. B. S.) reference tables. Tests of high-grade thermocouples at the National Bureau of Standards by Neville in 1923 (*2*) have shown that during a service test of 25 hours at 1500° to 1600° C., the e. m. f. (measured at 1200° C.) of the platinum element decreased 5.5 microvolts while that of the alloy element decreased 14.5 microvolts. The e. m. f. of the couple consequently decreased 9 microvolts at 1200° C. Neville also found that the corresponding decrease in the e. m. f. of thermocouples then made commercially was from 4 to 12 times as great (36 to 120 microvolts). The author has observed an average drop in the e. m. f. in this company's thermocouples at 1200° C. of less than 10 microvolts (less than 1° C.) after 36 hours at 1500° C. (uniform electrical heating in air).

The ability of the best thermocouples to retain their original characteristics when subject to high temperatures furnishes a basis for deciding how far it is worth while to go in tightening up on specifications. The limit is indicated as about ±1° C. Upon this basis and keeping in mind the fact that originally negative deviations from the standard values should not be permitted, a tolerance of +2° to 0° C. at 1200° C. as the maximum deviations from the 1933 reference tables will insure the utmost that can be obtained from platinum-rhodium thermocouples. These tolerances, therefore, form the basis for the essential requirements and shop specifications adopted. The fact that they are rigidly adhered to demonstrates that manufacturers may be reasonably expected to meet such close specifications.

Essential Requirements

Purity of Component Metals. The purity of the elements is of the utmost importance. The platinum, drawn into wire and electrically annealed for 3 minutes at 600° C., must have an e. m. f. of less than 10 microvolts against Pt 27 (the N. B. S. platinum standard) at 1200° C., and a temperature coefficient for the fundamental interval 0° to 100° C., $\frac{R_{100} - R_0}{100R_0}$ of 0.00392 or higher. (Table II.) This corresponds (*1*) to a purity of between 99.999 to 99.9999 per cent.

Rhodium must have a temperature coefficient of resistance between 0° and 100° C. of 0.00434 or higher. The temperature coefficient of electrical resistance is the most reliable test for purity.

Preparation of Wire. The platinum and the platinum-rhodium are melted in selected pure lime, following the usual procedure, using an oxy-hydrogen blow torch (with platinum tip), with strongly oxidizing flame. They are cast into ingots, forged, rolled, swaged, and finally drawn through diamond dies to size. The utmost care must be taken throughout the entire procedure to keep the material absolutely clean if contamination is to be avoided. The finished wire must be sound, uniform, smooth, and round. The maximum tolerance in size at finish is ±0.0002 inch.

Interchangeability and Reproducibility. Platinum can be made to meet closer specifications for interchangea-

bility than rhodium. The addition of slight impurities to pure platinum invariably makes it thermoelectrically more positive. The platinum is, therefore, practically always slightly positive to Pt 27 (the N. B. S. platinum standard). Occasionally a sample may be found which is 1 or 2 microvolts negative at 1200° C. to Pt 27 (indicating a purity very slightly higher than the Bureau's standard), but platinum is usually a few microvolts positive, although always by an amount less than 10 microvolts.

The e. m. f. of the platinum-rhodium wire, even when made up of impure constituents, can be adjusted for any one given temperature to any value within reason by changing the ratio of the constituents. At first sight this might seem to make high purity in the constituents a needless refinement. Such is not the case, however, for if impure constituents are combined in such a ratio that the resulting wire gives the e. m. f. in the standard table at 1200° C., it will not give the values in the standard table at other temperatures. It is for this reason that all the rhodium used by this company for thermocouple alloys is required to have a temperature coefficient of resistance, $\frac{R_{100} - R_0}{100R_0}$, of 0.00434 or higher.

The metals, both platinum and platinum-rhodium, must be homogeneous and as free from gases as possible. Homogeneity is much more easily achieved in platinum than in platinum-rhodium. In the latter, considerable segregation takes place and steps must be taken to reduce this to a minimum. The company's shop specification for homogeneity is that the difference in e. m. f., in either the platinum or the alloy wire, checked every 1.2 meters (4 feet) of the entire length of every coil (approximately 180 meters at 0.5 mm. diameter, 600 feet at 0.020 inch diameter) shall be less than 3 microvolts at 1200° C. Since the completed couple yields about 12 microvolts per degree Centigrade at 1200° C., this is the equivalent of 0.25° C.

The platinum-rhodium wire, of the degree of homogeneity specified above, is required to be between 0 and 24 microvolts plus to the company's standard alloy. This standard is one which combined with Pt 27 would exactly fit the standard table. Now, since the platinum is required to be between 0 and 10 microvolts plus to Pt 27, the deviation of the couple is always a quantity between 0 and 24 microvolts diminished by a quantity between 0 and 10. Thus if alloy wire is +12 microvolts and the platinum +6 microvolts, the completed couple will be +6 microvolts at 1200° C., or about 0.5° C. Numerous checks have shown the maximum deviation to average about 1° C. The maximum allowed for these departures on the completed thermocouple from the standard table is +24 to 0 microvolts or +2° to 0° C. at 1200° C. This figure represents the accuracy with which these couples can be used without calibration. Moreover the first effect of service is to decrease the e. m. f. and to bring the couple closer to the standard table.

Resistance to Contamination. Resistance to contamination of thermocouple wire during service is greatly affected by the temperature, time, and number of annealings before use. In service, the rate and extent of contamination of pure platinum annealed for 3 minutes at 1500° C. is about ten times that of 10 or 13 per cent rhodium-platinum similarly treated. Of the factors affecting the rate of contamination in service, temperature of anneal prior to use seems the most important.

The appearance under the microscope of highly annealed wire, especially pure platinum, is not dense but rather porous with large crystals, large open grain boundaries, and severe pitting. Such highly annealed wire is very susceptible to contamination in service. It seems that such wire is chemically or catalytically more active than wire annealed at lower temperatures. On the other hand the appearance of wire annealed at a low temperature is dense, not porous, and shows

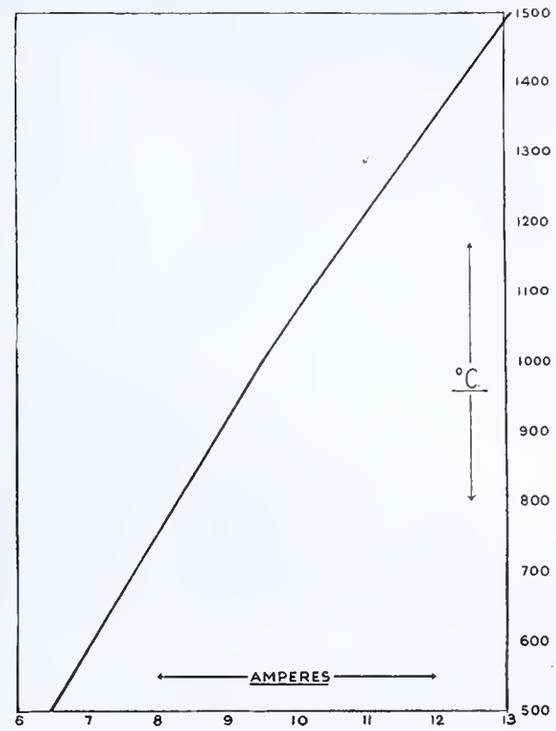

Figure 1. Temperature-Current Curve for Annealing Thermocouple Wire 0.05 Cm. Diameter

no recrystallization or grain boundaries. It is also mechanically much stronger, and less susceptible to contamination in service.

In the case of pure platinum and platinum-rhodium, the purpose of annealing is to normalize the wire. Knowing that wire annealed at a low temperature is less susceptible to contamination in service than wire annealed at a very high temperature, an investigation was started to determine the lowest possible temperature which would accomplish the desired result. It was found with pure platinum, annealed for 3 minutes at 600° C., that recrystallization takes place sufficiently to result in a constant e. m. f. and temperature coefficient of resistance. Magnification one hundred times does not show any visible signs of recrystallization. The grain size is considerably smaller than after annealing at higher temperatures and the density, strength, elongation, and general appearance of the wire are improved.

A similar condition exists for 10 per cent platinum and 13 per cent rhodium. Annealing for 2 minutes at 1200° C., instead of at 1500° C., as heretofore practiced, normalizes this wire sufficiently to produce constant e. m. f. values. The grain size of this wire also is considerably smaller than after annealing at higher temperatures. The strength, elongation, and general appearance also are improved.

Constancy of Calibration and Life

The usual procedure in making life tests is to suspend the wire between terminals and heat electrically to the desired temperature. The terminals should be close enough together to avoid putting the wire under any tension beyond that due to its own weight. Certain changes in e. m. f. values, general appearance, and mechanical properties appear after this annealing procedure. Thermocouples which are intended for accurate use should not be annealed at 1500° C., although a test at 1500° C. is a good criterion of their quality.

The wire which this company supplies commercially has been flash-annealed—that is, for 3 minutes—at 600° C., for the platinum and for 2 minutes at 1200° C. for the alloy. Before a melt is finally accepted, two samples, one from each end, are heated for 6 hours at 1500° C. and the maximum drop

Table I. Effect of Annealing

N. B. S. No.	Temperature	Current
	° C.	Amperes
5013	600	7.10
5014	800	8.30
5015	1000	9.52
5006	1100	10.20
5007	1200	10.93
5008	1300	11.66
5009	1400	12.39
5010	1500	13.12

Table II. Effect of Annealing

N. B. S. No.	Temp.	5-Minute Anneal: Thermal e. m. f.	5-Minute Anneal: $\frac{R_{100}-R_0}{100R_0}$	After 1 hour at 1450° C.: Thermal e. m. f.	After 1 hour at 1450° C.: $\frac{R_{100}-R_0}{100R_0}$
	° C.	Microvolts		Microvolts	
5013	600	−1	0.003923	+3	0.003922
5014	800	−1	0.003924	+3	0.003923
5015	1000	−2	0.003922	+3	0.003923
5006	1100	−1	0.003924	+1	0.003921
5007	1200	0	0.003921	0	0.003924
5008	1300	+1	0.003921	+1	0.003920
5009	1400	+1	0.003922	0	0.003920
5010	1500	+2	0.003922	+2	0.003920

Table III. Effect of Annealing Temperature and Time upon Tensile Strength and Elongation

Sample	Annealing		Tensile Strength[a]	Elongation
	° C.	Min.	Kg.	%
Thermocouple platinum	(Hard drawn, no anneal)		5.45	0.8
	600	3	2.95	36
	1000	3	2.61	34
	1200	3	2.50	34
	1500	3	2.27	32
	1500	1 hour	1.13	24
	1500	6 hours	.91	3.5
10% Rhodium platinum	(Hard drawn, no anneal)		11.80	0.6
	900	2	6.36	1.5
	1000	2	6.36	3.0
	1200	2	6.36	22.0
	1450	2	5.68	16.0
	1450	6 hours	2.72	6.0

[a] Kilograms at 0.5 mm. (0.020 inch) diameter.

from the flash-anneal to the 6-hour anneal at 1500° C. must not exceed 5 microvolts at 1200° C.

Experience has revealed an interesting phenomenon that occurs in such life tests. As time goes on the temperature near the terminals of the suspended wire becomes hotter, probably because of stretching due to the weight of the suspended wire and the fact that the rising currents of heated air make the temperature of the surrounding air hottest near the top. The ends, about 15 to 30 cm. (6 to 12 inches) are therefore disregarded. Samples of platinum wire annealed for 36 hours at 1500° C. show a drop of less than 5 microvolts and samples of 10 and 13 per cent alloy less than 10 microvolts under the same conditions (e. m. f. measured at 1200° C.). After 50 hours at 1500° C., the total drop of a thermocouple made of such wire is still less than 1° C. at 1200° C.

In order to determine the characteristics of pure platinum under different annealing conditions, a coil of wire of stock melt No. 26, 0.05 cm. (0.020 inch) in diameter was sent to the National Bureau of Standards. Eight samples of wire, each about 1.5 meters long, were cut from the coil and electrically annealed for 5 minutes in air, each wire at a selected temperature. These temperatures and the current required to bring the wire to the temperature in question, as reported by the National Bureau of Standards, are given in Table I, and plotted in Figure 1.

The e. m. f. versus Pt 27 and the temperature coefficients $\frac{R_{100}-R_0}{100\,R_0}$ were measured. All the samples were then heated electrically for 1 hour at 1450° C. and the e. m. f. and the temperature coefficient again determined. Table II gives the values reported by the National Bureau of Standards.

Each end of each sample was compared with Pt 27, and the Bureau of Standards reported that both ends gave identical results except in one case where the difference was 1 microvolt.

Mechanical Strength

Since the mechanical strength of the wire in service seemed to be very closely related to the annealing procedure before use, investigation was made to determine the best annealing practice. It was found that the lowest possible temperature for platinum is 600° C. and for platinum-rhodium 1200° C. These temperatures are sufficient to normalize the wire, and such wire has the greatest possible tensile strength (Table III) and also the greatest resistance to contamination in service.

Up to the present time, flashing at 1500° C. from 2 to 5 minutes and annealing at the same temperature from 1 to 6 hours has been generally believed to be essential and preferable, in order to establish the quality of thermocouples. It is possible to reduce the e. m. f. of platinum by such prolonged high-temperature treatment, but at the expense of the effective life in service. In the case of calcium contamination, for instance, it would be easily possible, by annealing at 1500° C., and faster yet at 1600° C., to reduce +25 microvolts to less than +10 microvolts against Pt 27, checked at 1200° C. The practice of burning out impurities, by prolonged high-temperature anneal, weakens the wire mechanically as well as renders it more susceptible to contamination, and such wire will not be nearly as satisfactory in actual service as platinum wire of less than 10 microvolts positive to Pt 27 at 1200° C., but which was annealed at the finish for 3 minutes at 600° C.

Conclusion

The tolerances of ±3 microvolts at 1200° C. for homogeneity within +2° to 0° C. for agreement with the standard values, and a maximum change of 5 microvolts at 1200° C., in the completed couple upon annealing for 6 hours at 1500° C. are, the author believes, the closest tolerances ever set up for thermocouples. Manufacturing experience with these tolerances demonstrates that they can be consistently met, however, and this fact should prove valuable to users of rare metal thermocouples as a guide in determining what performance they may reasonably demand.

Flash-annealing the platinum at 600° C. and the platinum-rhodium alloy at 1200° C. is sufficient to stabilize thermocouples of high quality. Intensive annealing does not materially change the e. m. f. and impairs the mechanical properties. Such annealing, moreover, renders the wire more susceptible to contamination during subsequent use.

Acknowledgment

Grateful acknowledgment is made for the helpful coöperation of H. T. Wensel and W. F. Roeser of the National Bureau of Standards for determining the data given in Tables I and II, and A. O. Ashman and C. F. Homewood of the New Jersey Zinc Company.

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(2) Neville, R. P., *Trans. Am. Electrochem. Soc.*, **43**, 371 (1923).
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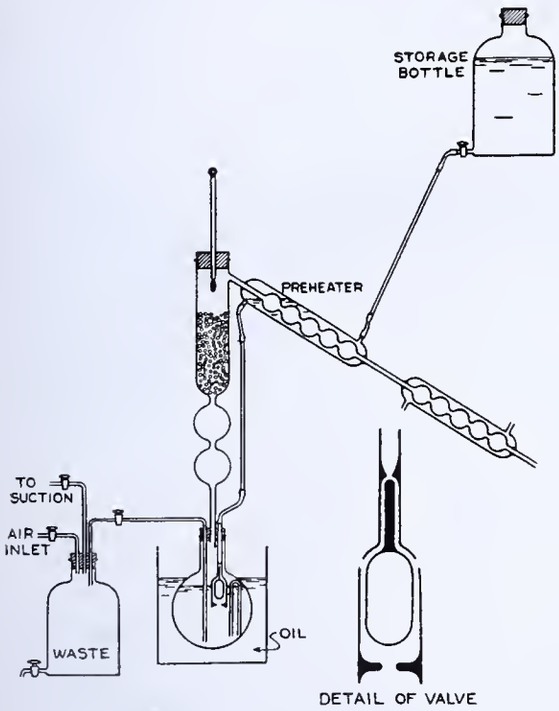
Received May 18, 1935.

An Economical Continuous Distilling Apparatus

FRANK M. SCHERTZ, 1305 Farragut St., N. W., Washington, D. C.



THE recovery of large quantities of solvents in isolating carotene, chlorophyll, and xanthophyll led to the development of the distilling apparatus illustrated. It was economical of heat and practically eliminated all danger of fire.

The storage bottle which contained the solvents to be distilled was elevated high enough so that gravity alone caused the liquids to flow into the distilling flask, after passing through a condenser which was used as a preheater. The storage bottle could be placed at a distance from the still and thus reduce the fire hazard.

The flow of solvent into the distilling flask was controlled by means of an automatic float (3.5 × 6 cm.) which kept it at a constant level during distillation. The end of the glass rod (5 mm. × 5 cm.) which was part of the valve was ground into the modified inlet tube, so that a seal was made when the liquid in the distilling flask caused the float to rise. The parts were constructed as illustrated, so that they would not stick. Holes were made in the top of the cage (4 × 8 cm.) of the valve so that the air would not be trapped and prevent the float from rising.

The 3-liter distilling flask contained an inverted U-shaped small-bore (2-mm.) glass tube to eliminate bumping as well as a glass tube extending to the bottom of the flask through which waste liquors could be siphoned off.

The oil bath was made of copper, silver-soldered at the seams. Nujol or any oil with a high flash point may be used in the bath. In recovering methanol or acetone from an aqueous solution the temperature of the bath often ran as high as 170° C.

Using a 1000-watt hot plate of the open type with a three-heat switch control, 2.5 liters of 95 per cent ethanol were distilled in 1 hour. Solvents with boiling points between 20° and 100° may be easily distilled or recovered.

Acknowledgments

Indebtedness is due Carl Rist for suggesting the use of a float for maintaining the constant level of the liquid in the distilling flask, Arthur Mack for its construction, and Mrs. Constance Sherry for the drawing.

RECEIVED June 29, 1935.

An Automatic Still Cut-Off

ARTHUR H. HALE AND FRED D. TUEMMLER

T. Jefferson Coolidge, Jr., Memorial Laboratory, Harvard University, Cambridge, Mass.

A SIMPLE fool-proof automatic switch for breaking the circuit to an electrically heated Barnstead conductivity water still was needed to prevent any possibility of burning out the heating units by boiling the still dry.

Either an outside or inside float switch seemed impractical, since positive action might not always be certain in alkaline permanganate from which the water was distilled. By calibrating the rate of distillation on the glass level indicator in terms of the drop in the water level in 15-minute intervals, it was possible to use a time-clock switch to operate a magnetic switch controlling the still. However, if the magnet was controlled only by the clock switch, the still would turn on automatically at 12-hour intervals, or if the current stopped even momentarily, the clock would stop until started again manually but the still circuit would be closed again when the current returned without any possibility of being opened by the clock. In either case there was no protection against burning out the heating units.

To solve this problem the circuit in Figure 1 was used, the important feature of which is the momentary switch. Since the magnetic switch is held in contact through one of its own arms, a momentary interruption of the current will open it. To close the magnetic switch, the momentary switch is connected across the gap in the magnet circuit and only by pushing this switch can the still circuit be completed once it is opened. This circuit is applicable for use with any electrically operated machine which must not operate beyond a certain time limit and which must not again operate after the 12-hour interval of the clock.

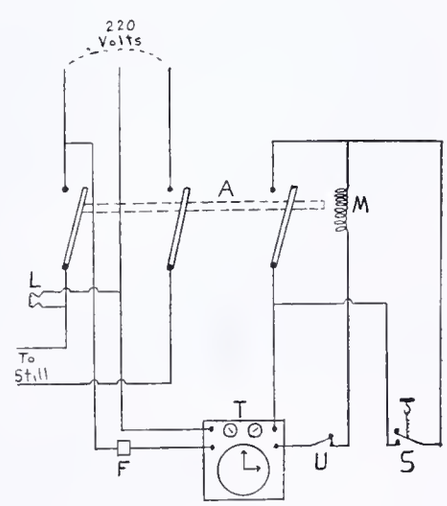


FIGURE 1. WIRING DIAGRAM

A. Magnetic switches
F. Fuse (110 volt)
L. Pilot light
M. Magnet
S. Momentary switch
T. Time-clock switch
U. Manual cut-off switch (ordinarily left closed)

RECEIVED September 21, 1935.

Carbon Dioxide from Dry Ice

WALTER S. IDE

Burroughs Wellcome and Company, U. S. A., Experimental Research Laboratories, Tuckahoe, N. Y.

IT HAS been found that carbon dioxide gas, generated from the solid in a convenient apparatus, is a very satisfactory source of carbon dioxide for use in the determination of nitrogen by the micro-Dumas method. Carbon dioxide snow is now becoming readily available in most laboratories.

The solid carbon dioxide in small pellets is placed in the mercury trap, which is a test tube 20 mm. in diameter and 20 cm. long, fused to another tube of like dimensions (Figure 1). The open end of the tube is fitted with a stopper containing a stopcock. A few minutes after introduction of the pellets the air in the trap will all be expelled. By closing stopcock *A*, the gas will be forced into the 8- to 10-liter aspirator bottle which has been filled with freshly boiled water and may be graduated to measure the quantity used. The water is forced out through special nitrometer tubing into a large thick-walled rubber bladder (heavy beach ball).

On setting up the apparatus, it is convenient to flush the aspirator bottle and bladder with carbon dioxide from a tank, filling the bladder with water before connecting to the bottle. The water will then flow into the bottle until it is filled and the bladder is deflated, ready to receive the carbon dioxide as it is generated. The bladder should be placed on a shelf approximately level with the top of the aspirator bottle. This height should be adjusted so that there will be positive internal pressure at all times.

The carbon dioxide should be released and replaced several times. This will insure very small microbubbles in the azotometer; in fact, the bubbles obtained appear to be smaller than those obtained by any other source. After some weeks the size of the bubbles increases very slightly. It is good practice to refill the generator about once each week during routine work to eliminate the possibility of this error.

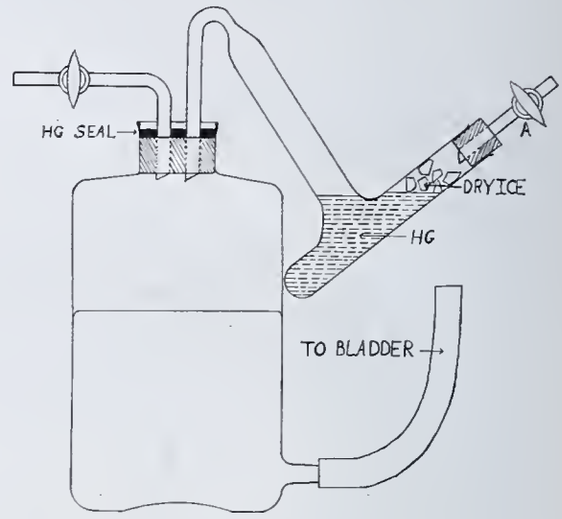


FIGURE 1

The method was suggested by J. S. Buck of this laboratory.

RECEIVED August 7, 1935.

Stirring Air within Desiccators

FRANK J. ZINK, Kansas Agricultural Experiment Station, Manhattan, Kan.

A NUMBER of investigators have used sulfuric acid solutions as a means of humidity control within small enclosed spaces. Wilson (*2*) suggested the use of desiccators for humidity chambers in conjunction with equilibria moisture determinations and pointed out the desirability of keeping the enclosed air in motion. However, Wilson (*2*) and Wilson and Fuva (*3*) did not use desiccators in their many equilibrium moisture determinations, possibly because the stagnant air resulted in a low rate of interchange of moisture. Lindsay (*1*) also pointed out the undesirability of such determinations in stagnant atmospheres.

Obviously, any mechanical means of stirring air within desiccators would be difficult to arrange and might interfere with the normal convenient use of the desiccator. The author has evolved a simple means of stirring air within desiccators, and presents it with the hope that others may find it useful in similar applications. Small fans mounted on pivots inside the desiccator were induced to rotate by a series of mechanically moved permanent magnets passing near the outside of the desiccator. The equipment was used in a series of investigations of equilibria moistures of forage hays and grains, in which 15 desiccators, each with enclosed fan, were used.

Figures 1, 2, and 3 illustrate the apparatus, the cost of which, exclusive of motor, was approximately $15. Many laboratories already have most of the apparatus available.

Metal desiccator plates were substituted for the usual porcelain plates. Small pivots were made, as illustrated in Figure 2, of steel wire about 0.0625 inch in diameter and 3 inches long and were soldered to the edges of the plates. The upper end was bent in such a manner as to offset it toward the center of the plate, so that the entire area of the plate would be free for moisture dishes. The ends of the pivots were sharpened to a point.

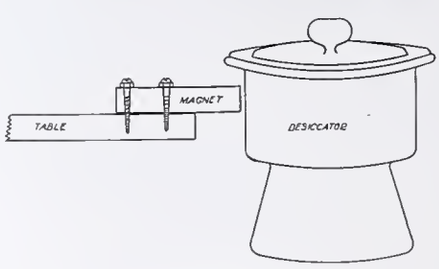


FIGURE 1

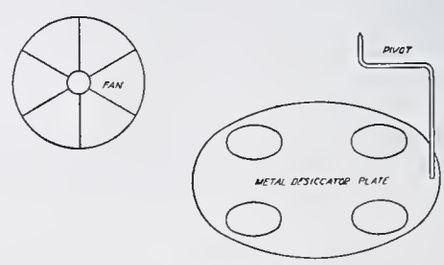


FIGURE 2

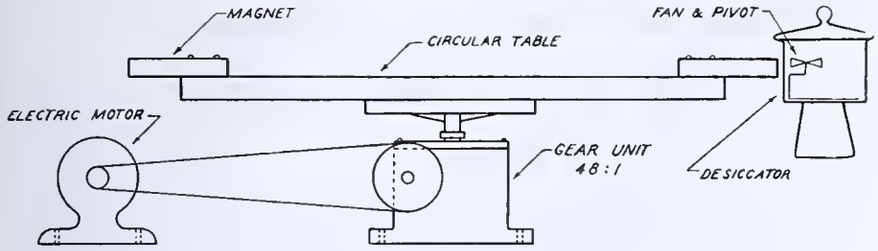


FIGURE 3

Sheet-metal tin disks 2.5 inches in diameter were cut and punched at the center with an ordinary center punch, care being used not to puncture the metal, to serve as the socket of a pivot bearing. Six radial cuts 1 inch deep were made in the edge with tin shears, and the segments were bent to serve as fan blades. These fans were then balanced on the pivots and the unit was placed inside the desiccator, so that the fans when in place just cleared the side. The fan may be lifted off the pivot and laid aside for removal or insertion of the sample dishes. With this type of pivot the fans rotated freely and were induced to rotate by magnets passing near the outside of the desiccator and on a level with the fan. The electromagnetic flux permeating the glass induced the fan to rotate, and no mechanical connection to the fan was necessary.

The motive power was furnished by a series of motor car magneto-magnets mounted on a circular platform, on a Boston Gear Company show window display unit of 48 to 1 ratio. An 1800-r. p. m., 0.125-h. p. electric motor was belted directly to the gear unit. A 2.5-foot diameter platform furnished ample space for 15 desiccators placed in a circle concentric with the platform and just outside the circle created by the passage of the magnets. The magnets were passed at the rate of 8 feet per minute and the more freely moving fans rotated at approximately 200 revolutions per minute.

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A Molecular Still

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IN THE course of the purification of the corpus luteum hormone, progestin (*3*), it was found necessary to subject the highly purified concentrate to distillation in a molecular still. Since the described devices designed for use with small quantities were not entirely satisfactory for this purpose, a new type of apparatus modeled after the molecular still of

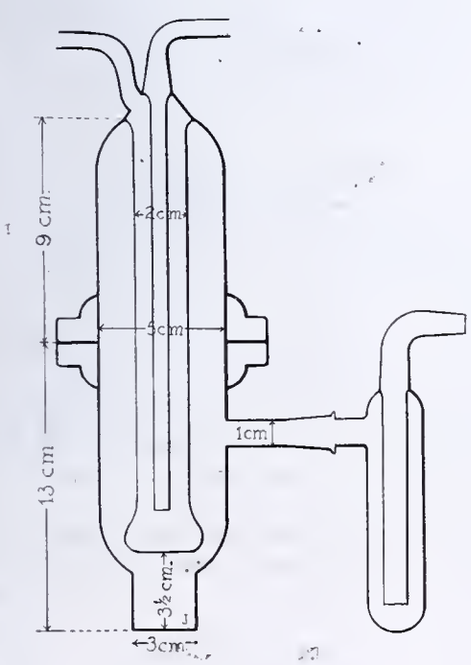

FIGURE 1

Carothers and Hill (*1*) was designed. The still has the advantage that, in addition to being readily charged and cleaned, the temperature of distillation may be simply controlled.

The still (Figure 1) was constructed from two pieces of old-style, flanged Pyrex pipe, 15 × 5 cm., the final dimensions being given in the diagram. After the apparatus was fabricated it was annealed and the surfaces ground for high-vacuum work. The still was heated by means of a small oil bath placed around the well of the apparatus.

In operation the thick oil to be distilled is dissolved in a small amount of ether and transferred by pipet to the well. The solvent is removed by cautious warming or by an air jet and the last traces by evacuation—first with a water pump and then with an oil pump. During this preliminary evacuation the condensing part of the apparatus is not used, the upper end being closed with a rubber stopper. Finally, when it is apparent that easily volatile substances have been removed, the stopper is replaced by the condenser, and the apparatus, including the trap, is attached to the intake of a mercury vapor pump. With the joints well greased and the mercury pump trapped with solid carbon dioxide, a vacuum of 0.0002 mm. is attained in a very short time, providing no distillation is taking place. By slowly heating the oil bath surrounding the well the distilling temperature is reached without any visible boiling and a waxy substance soon collects on the pestle from which it can be removed by immersion in benzene or other suitable solvent. A well of the size used will accommodate from 1 to 2 grams without difficulty. The detailed set-up of the high-vacuum apparatus and the technic of operation were essentially those described by Hickman and Sanford (*2*).

This same apparatus has been used for the purification of a number of other products of biological origin and appears to be adapted to a large variety of conditions.

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RECEIVED August 29, 1935.

A Simple Reflux Condenser for Use with Erlenmeyer Flasks

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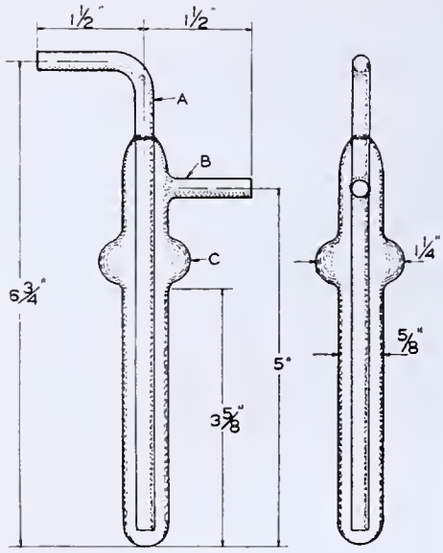

FIGURE 1

DURING the course of a study on the saponification number determination of oils the authors felt the need of a reflux condenser which could be conveniently used in an ordinary Erlenmeyer flask. Such a condenser as shown in Figure 1 was made up from an ordinary 150 × 16 mm. test tube and 8-mm. glass tubing and proved so satisfactory that others of like construction have been used for boiling various solutions under refluxing conditions.

The condensers can be made by anyone familiar with glass-blowing technic by taking an ordinary test tube of such diameter that it will loosely fit in the Erlenmeyer flask to be used, and sealing in tube *A*. Section *C* is then enlarged as shown to act as a support for the condenser in the flask and tube *B* sealed in. The condensers can be used individually, or in series as shown in Figure 2 by means of appropriate rubber tubing connections. The dimensions shown in Figure 1 are suitable for condensers for standard Erlenmeyer flasks of 250-cc. capacity. Other sizes can be used for flasks of different dimensions.

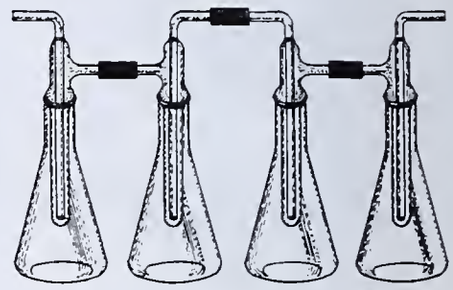

FIGURE 2

RECEIVED September 9, 1935.

An Improved Liquid Absorption Tube

W. D. TURNER, Columbia University, New York, N. Y.

AN IMPROVED absorption bulb for dry absorbents, such as ascarite, recently described (*1*), has now been supplemented by a similar tube for liquid absorbents. The new unit consists of the solid absorption tube, to which has been added the familiar Friedrichs gas absorption principle, in the form of a helical coil. This unit possesses all the advantages of the original dry absorber, besides offering a contact path of some 42 cm. in length between the gas bubbles and the liquid absorbing medium.

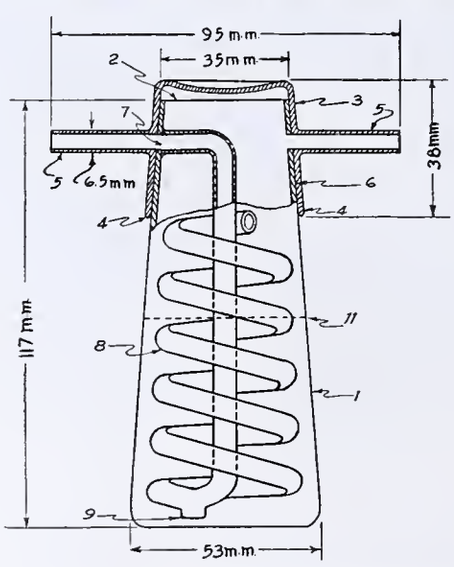

FIGURE 1. LIQUID ABSORPTION BOTTLE

Round glass body 1, 2; external stopper, 3, 4; lateral tubes, 5; ground joint, 6; tube and coil attached to inner side of body neck, 7, 8; open foot of coil, 9; hole communicating with top interior, 10; liquid level in charging, 11.

The advantages of this outfit over other familiar designs are:

Minimal outside surface: easy to wipe to constant weight.
Minimal parts: one body, one stopper, one ground joint.
Minimal surface contour: low breakage.
Simple, positive operation: one turn of one stopper shutting inlet and outlet short off.
Minimal waste space: larger capacity completely utilized.
Stable standing.
Light weight.
Ground joint external: not contaminated in charging.
Simple construction: low cost.

In practice, this liquid absorber is followed in the combustion train by a Turner absorption bottle for solids in the customary arrangement for taking up any moisture volatilized from a liquid absorbent.

Absorbers of this type are in satisfactory use at Columbia University, and have been readily made to order by the glass-blowing departments of Eimer and Amend and others.

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RECEIVED November 1, 1935.

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